HYDROGEN IONS

THEIR DETERMINATION AND IMPORTANCE IN PURE AND INDUSTRIAL CHEMISTRY

by

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BEING VOLUME THREE OF A SERIES OF MONOGRAPHS ON APPLIED CHEMISTRY

Founded by the late

E. HOWARD TRIPP, Ph.D.

To E. B.

EDITORIAL PREFACE

IN these days of intensive and extensive research, every worker in science or its applications knows how rapidly the contents of text-books and encyclopædias become out of date; and those who wish to see new work published know the difficulties which abnormal taxation and high labour costs offer to the realisation of their desire. The one obvious solution of the problem is the publication of monographs that would focus attention upon recent work, or upon new aspects of old work, and upon their theoretical implications. Such books are usually written by experts for other experts in related fields of science, or for the well-educated layman whose thirst for new knowledge has not been quenched by the more sensuous outpourings of the ephemeral press.

It is interesting at times to speculate upon what aspects of our civilisation the future historian will select as the most characteristic of our time. Scientific discoveries and their application to human welfare, we may be sure, will find a place; and to these many will add the growth of our sense of " values." The value of new work in science varies greatly: the golden grain is always accompanied by chaff, and there is no precious ore without country rock. Owing to the difficulty of assessing the value of work at the time of its production, we find that our scientific periodicals stand in danger of being swamped by the mass of second- and third-rate material that is thought to be worth publishing, but which posterity will decree would have been better left in manuscript form. It is the first duty of the monograph writer to estimate the value, either actual or potential, of recent work upon the subject of which he writes: he must pick out the plums to save others from the indigestion that follows eating the whole pie. Further, in addition to being

accurate, his work must be presented in a form that is both assimilable and attractive ; in other words, he must show that lucid exposition can be achieved by the use of few words, if they are rightly chosen, and that attractive presentation is attained rather by clear thinking than by superficial display.

The present series of monographs has been designed with these objects and ideals in view. The task which the authors have been set is no easy one ; so that should performance occasionally fall short of intention, the critical reader is asked to echo the words of Goethe that " higher aims, even if unfulfilled, are in themselves more valuable than lower aims quite attained."

E. HOWARD TRIPP

AUTHOR'S PREFACE

HYDROGEN-ION concentrations have long been recognised as an essential factor in many biochemical processes, and it is undoubtedly on account of this recognition that considerable additions have been made in recent years to our knowledge of biochemical principles. In other branches of chemistry, hydrogen-ion concentrations are only just beginning to be regarded as being of fundamental importance, and the use of the hydrogen electrode and the other associated methods are being increasingly applied, not only to measure very small changes in acidity and alkalinity, but as valuable indicators of the extents to which reactions have proceeded and as a means of controlling these reactions with an exactitude hitherto impossible. This also applies to various manufacturing processes.

In writing this book the author has endeavoured: firstly, to provide a practical discussion of the various electrometric and colorimetric methods of determining the concentration of hydrogen ions; secondly, to show the fundamental importance of hydrogen-ion concentrations in general chemistry, including volumetric and gravimetric analytical procedures; and, finally, to indicate the important rôles played by hydrogen-ion concentrations in numerous industrial chemical processes, and how the various methods of measuring hydrogen-ion concentrations have been employed for the purpose of control. In order to elucidate the importance of hydrogen-ion concentrations in manufacturing processes to the general reader, brief outlines of the processes have been included wherever they were considered necessary.

Methods of very limited application of determining concentrations of hydrogen ions, such as those depending on the rate of

A*

catalytic decompositions, and conductivity measurements have been excluded, in view of the marked superiority of the methods described in the book.

As is well known, much controversy is taking place as to the mode of ionisation of strong electrolytes. Unfortunately, the degree of ionisation, if considered in terms of the *concentration* of ions, leads to one standard with which electrode potentials are compared, whereas, if considered in terms of the *activity* of ions it leads to a slightly different standard. In view of there being no really satisfactory theory of solutions incorporating their many properties, the author has deemed it advisable to adhere to the more usual ion-concentration theory in the interpretation of electrode potentials. Discussions of the theories of G. N. Lewis and Debye and Hückel have been considered to be outside the scope of this book, and they should be sought in treatises on physical chemistry or in the original literature. Whatever may be the true interpretations of the potentials of the hydrogen electrode, and of the other electrodes which have been standardised against it, one thing is certain that the voltages constitute a remarkable and delicate means of registering and controlling acidity and alkalinity.

The author gratefully acknowledges his indebtedness to Mr. A. G. Pollard, B.Sc., A.R.C.S., D.I.C., Lecturer in Agricultural Chemistry in the Imperial College of Science and Technology (Royal College of Science), London, for writing the greater portion of the chapter on the " Fertility of Soils " ; a subject on which he and his students have been actively carrying out research for the past few years. The author's best thanks are also due to the Editor of *The Industrial Chemist*, for kind permission to reproduce much material and for the use of the appropriate blocks of the diagrams, which first appeared in the author's articles in that invaluable journal ; to the Chemical Society for kind permission to reproduce several of the diagrams which were published in the author's original papers in the Society's Journal ; and to Messrs. A. Gallenkamp & Co., Ltd., London, Messrs. Cambridge Instrument Co., Ltd., London, Messrs. The British

PREFACE TO THIRD EDITION

OWING to the incidence of the War, the publication of a new edition of " Hydrogen Ions " has been somewhat delayed. The years which have intervened since the Second Edition appeared have been marked by a considerable increase in the original literature on pH, not only in regard to chemistry, but in regard to its many industrial applications. Nevertheless, the author has made every effort to bring the treatise up to date, and this has necessitated the incorporation of several new chapters. The whole text has been revised and substantial additions have been made throughout. In consequence of the much increased size, it has been deemed desirable to publish the work in the form of two volumes. The first volume deals mainly with the theory and methods of determining hydrogen-ion concentration, or activity, and the second, chiefly with the part played by hydrogen ions in chemistry and in its numerous technical processes.

As much of the fundamental work on hydrogen ions was carried out before the activity theory of electrolytes had gained wide acceptance, and as the electrometric determinations of pH are usually made with cells in which *liquid junctions* exist and to which the modern theory is not strictly applicable, the theoretical interpretation of the E.M.F. of such cells, given in the earlier editions, has been retained. To some, this procedure might appear unjustifiable, but the fact must not be lost sight of that the activity theory can only be rigidly applied to cells *without transport, i.e., without a liquid junction*, which type of cell is scarcely ever used for ordinary pH determinations. Whatever may be the true meaning of the pH value, there is no doubt that pH values will remain an invaluable means of accurately assessing the extent of the acidity or alkalinity of a solution.

A chapter was inserted in the Second Edition on the inter-

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VOLUME TWO

CHAPTER XXII

THE INFLUENCE OF HYDROGEN-ION CONCENTRATION ON OXIDATION-REDUCTION PROCESSES. rH

ORIGINALLY it was considered that reduction was essentially a process in which nascent or atomic hydrogen was involved. Thus the reduction of ferric ions might be regarded to follow the equation :—

$$Fe''' + H \dashrightarrow Fe'' + H^{\cdot},$$
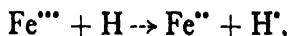
and oxidation of the ferrous ions by the reverse process

$$H^{\cdot} + Fe'' \dashrightarrow H + Fe'''.$$

Reasoning along these lines, the reduction of ferric ions by stannous ions :—

$$2Fe''' + Sn'' \dashrightarrow 2Fe'' + Sn''''$$
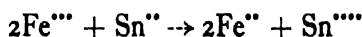
might be regarded as the outcome of two processes :—

(a) $2Fe''' + 2H \dashrightarrow 2Fe'' + 2H^{\cdot}$
(b) $Sn'' + 2H^{\cdot} \dashrightarrow Sn'''' + 2H$
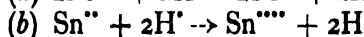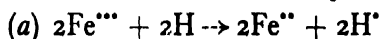
in which the hypothetical two atoms of uncharged hydrogen involved in reduction (a) are returned to the solution again by virtue of the oxidation (b). In actual fact, the reduction occurs spontaneously, without the participation of either hydrogen atoms or ions. Consideration of the normal oxidation-reduction potentials, *viz.*, $\varepsilon_{0_{Fe'' \to Fe''}} = + 0.75$, $\varepsilon_{0_{Sn''' \to Sn''}} = - 0.15$, shows that the reaction involves an appreciable degradation of energy, or in other words, the reaction can perform maximum external work, or else the reactants may be regarded as possessing available free energy which as the reaction proceeds may be converted into work. This may be expressed thus :—

$$2Fe''' \dashrightarrow 2Fe'' + 2FE_{Fe'' \to Fe''}$$
$$Sn'''' \dashrightarrow Sn'' + 2FE_{Sn''' \to Sn''}$$

whence

$$2Fe''' + Sn'' \dashrightarrow 2Fe'' + Sn'''' + 2F(E_{Fe'' \to Fe''} - E_{Sn''' \to Sn''})$$
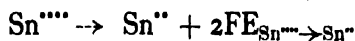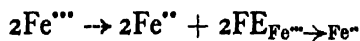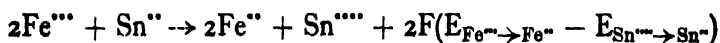
where

$$2F(E_{Fe'' \to Fe''} - E_{Sn''' \to Sn''}) = -\Delta F \text{ (free energy)}$$
$$= A \text{ (maximum work)}.$$

In some oxidation and reduction processes, however, hydrogen ions are integral reactants in the systems, *e.g.*, oxidations effected with $KMnO_4$, $K_2Cr_2O_7$ and $KBrO_3$, thus :—

$$MnO_4' + 8H^{\cdot} \rightarrow Mn^{\cdot\cdot} + 4H_2O + 5F.E_{MnO_4' \rightarrow Mn^{\cdot\cdot}}$$
$$HCrO_4' + 7H^{\cdot} \rightarrow Cr^{\cdot\cdot\cdot} + 4H_2O + 3F.E_{HCrO_4' \rightarrow Cr^{\cdot\cdot\cdot}}$$
$$BrO_3' + 6H^{\cdot} \rightarrow Br' + 3H_2O + 6F.E_{BrO_3' \rightarrow Br'}$$
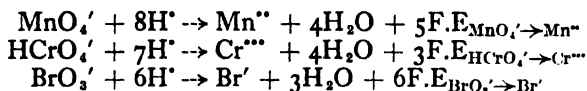
There is also a number of instances of the oxidation or reduction of organic bodies, in which although hydrogen ions do not actually take part in the oxidation-reduction process, they are indirectly involved through the ionisation of one of the reactants. As an example, we may consider the system involved in the quinhydrone electrode. The actual reactants are quinone and its reduced form, the doubly charged anion of hydroquinone, thus :—

(Q)   (Q'')
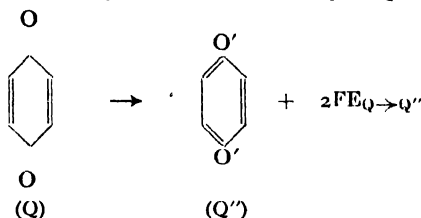
As shown on page 23, Vol. I, the concentration of hydroquinone anions is governed by the two dissociation constants of hydroquinone and by the hydrogen-ion concentration of the solution. The potential set up at a platinum electrode immersed in a solution—the total concentrations of quinone and hydroquinone of which are respectively [quinone] and [hydroquinone]—is

$$E_{Q \rightarrow Q''} = r_{Q \rightarrow Q''} - \frac{RT}{2F} \log_e K_1 K_2 - \frac{RT}{2F} \log_e \frac{[\text{hydroquinone}]}{[\text{quinone}]}$$
$$+ \frac{RT}{2F} \log_e ([H^{\cdot}]^2 + K_1[H^{\cdot}] + K_1 . K_2).$$

Applying this formula to the special case of the quinhydrone electrode for which [hydroquinone] = [quinone], it was shown

that
$$E_{\text{Quin.}} = \lambda + \frac{RT}{F} \log_e [H^{\cdot}]$$

when $[H^{\cdot}]$ was not greater than 10^{-7}. Application to alkaline solutions, $pH > 7$, is not possible owing to the air-oxidation of the hydroquinone which then occurs.

We shall now consider similar examples of the reduction process :

$$\text{Ox (Oxidant)} \rightarrow \text{Red'' (Reductant'')} + 2F.E_{Ox \rightarrow Red''}$$

which unlike the quinone-hydroquinone system, sets up the potentials set up at a platinum electrode that can be measured over the complete pH range. The potential, $E_{Ox \to Red''}$, may therefore be represented by the expression

$$E_{Ox \to Red''} = \varepsilon_{Ox \to Red''} - \frac{RT}{2F} \log_e K_1 K_2 - \frac{RT}{2F} \log_e \frac{[Red]}{[Ox]}$$

$$+ \frac{RT}{2F} \log_e ([H^{\cdot}]^2 + K_1 . [H^{\cdot}] + K_1 . K_2)$$

$$= \varepsilon'_{Ox \to Red''} - \frac{RT}{2F} \log_e \frac{[Red]}{[Ox]}$$

$$+ \frac{RT}{2F} \log_e ([H^{\cdot}]^2 + K_1 [H^{\cdot}] + K_1 K_2)$$

where $\quad \varepsilon'_{Ox \to Red''} = \varepsilon_{Ox \to Red''} - \dfrac{RT}{2F} \log_e K_1 K_2.$

The validity of this expression may be tested experimentally. By introducing equal molecular amounts of oxidant and reductant, *i.e.*, [Ox] = [Red], into solutions of different pH, graphs may be drawn connecting the potentials set up at a platinum electrode and pH. Such curves are given in Fig. 94 for quinhydrone, the four sulphonates of indigo and anthraquinone β-sulphonate, at 30° C., these substances being present with equimolecular amounts of their respective reduced forms. It will be seen that the initial slopes of these curves are all $- 2 \cdot 3026 RT/F$ and is thus the same as that of the graph representing the variation in the potential of the hydrogen electrode with increasing pH. At pH values above 8, the slopes of the indigo sulphonates become $- 2 \cdot 3026 RT/2F$. This is also true of the anthraquinone β-sulphonate curve, but above pH 11·5 the slope changes to zero. These different slopes are in accord with theory as the following considerations show. The second slope, $- 2 \cdot 3026 RT/2F$, is caused by the primary ionisation of the reductant becoming the predominating factor, whereas the " zero " slope begins when the secondary dissociation begins.

When [Ox] = [Red], and (i) [H$^{\cdot}$] is large compared with either K_1 or K_2,

$$E_{Ox \to Red''} = \varepsilon'_{Ox \to Red''} + \frac{RT}{F} \log_e [H^{\cdot}],$$

$$= \varepsilon'_{Ox \to Red''} - \frac{2 \cdot 3026 RT}{F} p\mathrm{H} \, ;$$

(ii) [H$^{\cdot}$] is large compared with K_2 (*i.e.*, the term $K_1 K_2$ becomes negligible), but not when compared with K_1, then

$$E_{Ox \to Red''} = \varepsilon'_{Ox \to Red''} + \frac{RT}{2F} \log_e ([H^\cdot]^2 + K_1[H^\cdot]).$$

As the pH increases, so $[H^\cdot]^2$ will eventually become negligibly small compared with $K_1[H^\cdot]$, whence

$$E_{Ox \to Red''} = \varepsilon'_{Ox \to Red''} + \frac{2 \cdot 3026 RT}{F} \log_{10} K_1 - \frac{2 \cdot 3026 RT}{F} pH,$$

the slope then becoming $- \dfrac{2 \cdot 3026 RT}{F}$;

(iii) $[H^\cdot]$ is small compared with either K_1 or K_2, then

$$E_{Ox \to Red''} = \varepsilon'_{Ox \to Red''} + \frac{RT}{2F} \log_e K_1 K_2,$$
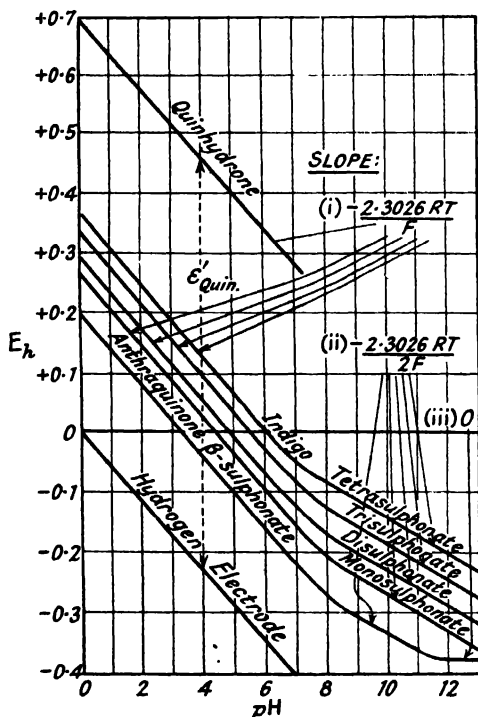
FIG. 94.—Showing the different Slopes given by Platinum Electrode Potentials, E_h, $-p$H Curves of half-reduced Quinone, Indigo Sulphonates and Anthraquinone β-Sulphonate.

(Sullivan, Cohen and Clark, *U.S. Hyg. Lab. Bull.* No. 151, p. 82, 1928 ; Conant, Kahn, Fieser and Kurtz, *J. Amer. Chem. Soc.*, 1922, **44**, 1382).

from which it is seen that the potentials, E, then remain constant even though the pH is increased, thus explaining the zero slope exhibited by anthraquinone β-sulphonate.

Unfortunately, dyestuffs on being reduced to their leuco bases do not generally follow such a simple relationship as that outlined above owing to the presence of basic and acid groupings, both sometimes existing in the same molecule. The possibility of such ionisations render the mathematical interpretation of E_h/pH curves of half-reduced dyestuffs exceedingly difficult.
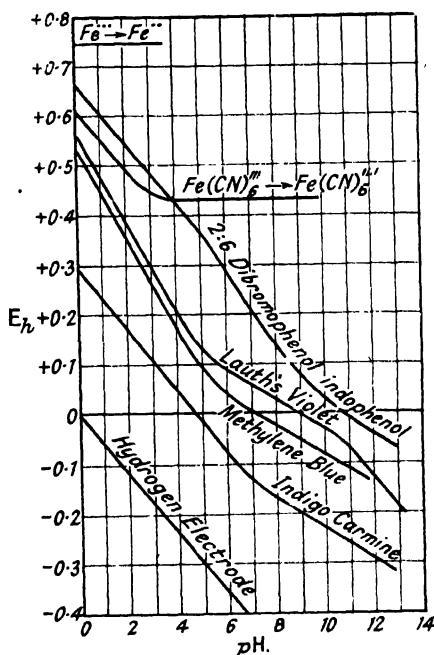
FIG. 95.—E_h/pH Curves of Half-reduced Dyestuffs, and of Ferricyanide. (Clark, Cohen and Gibbs, *U.S. Hyg. Lab. Bull.* No. 151, p. 197, 1928.)

Examples of such curves are those of methylene blue and Lauth's violet given in Fig. 95.

Table 156 gives the normal oxidation-reduction potentials of the more important processes. In it are also included normal electrode potentials, for they refer to reduction systems in which the reductant is the metal and the oxidant the metal-cation. They represent the potentials set up at a metal electrode when in equilibrium with its ions at a concentration of 1 g.-mol. per litre, or, considered from the standpoint of the activity theory, when

the solution contains the ions at unit activity. The latter concept, however, involving a different mathematical computation, results in slightly different values being obtained. The potentials of the systems indicated on the right of Table 156 are obtained from the E.M.F's of cells, one-half element being a platinum electrode dipping in a solution of the system and the other being a suitable standard half-element, *e.g.*, one of the calomel electrodes, the two electrodes being connected with a salt bridge of a saturated solution of potassium chloride. Both the normal electrode and " Redox " potentials are referred to the normal hydrogen electrode as being of the standard, but arbitrary, zero potential.

<div align="center">

TABLE 156

NORMAL OXIDATION-REDUCTION POTENTIALS (N-H = 0)

</div>

Au· → Au .	1·50	Co··· → Co··	1·82
Au··· → Au	1·36	Pb···· → Pb··	1·75
Hg·· → Hg	0·86	Mn···· → Mn··	1·64
Hg₂·· → 2Hg	0·80	MnO₄′ + 4H· → MnO₂	1·64
Ag· → Ag	0·80	Ce····· → Ce···	1·60
Tl· → Tl .	0·72	Mn··· → Mn··	1·58
Cu· → Cu .	0·51	MnO₄′ + 8H· → Mn··	1·50
Cu·· → Cu	0·34	ClO₃′ + 6H· → Cl′	1·44
Bi··· → Bi .	0·23	BrO₃′ + 6H· → Br′	1·42
Sb··· → Sb.	0·1	HCrO₄′ + 7H· → Cr···	1·30
H· → H	0	Tl··· → Tl·	1·22
Fe··· → Fe	− 0·4	IO₃′ + 6H· → ½I₂	1·20
Sn·· → Sn .	− 0·10	VO₂· + 2H· → VO··	1·00
Pb·· → Pb .	− 0·12	NO₃′ + 4H· → NO	0·95
Ni·· → Ni .	− 0·22	2Hg·· → Hg₂··	0·95
Zn·· → Zn	− 0·76	Fe··· → Fe··	0·75
Mg·· → Mg	− 1·55	MnO₄′ → MnO₄′′	0·66
Na· → Na .	− 2·71	H₃AsO₄ + 2H· → H₃AsO₃	0·61
		Fe(CN)₆′′′ → Fe(CN)₆′′′′	0·44
½ Cl₂ → Cl′	+ 1·36	Cu·· → Cu·	0·16
½ Br₂ (aq.) → Br′.	+ 1·09	Ti···· → Ti···	0·06
½ I₂ → I′	+ 0·62	Sn···· → Sn··	− 0·15
		Cr··· → Cr··	− 0·41

<div align="center">

Case I

</div>

Systems of the type :

$$M^{\cdots m} \dashrightarrow M^{\cdots n} + (m - n)FE_{M^m \to M^n}$$

or

$$Ox \dashrightarrow Red + (m - n)FE_{M^m \to M^n}$$
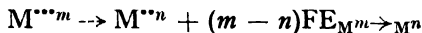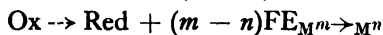
$$E_h = \varepsilon_{M^m \to M^n} - \frac{RT}{(m - n)F} \log_e \frac{[Red]}{[Ox]}.$$

$$= \varepsilon_{M^m \to M^n} - \frac{0\cdot058}{m - n} \log_{10} \frac{[Red]}{[Ox]} \text{ at } 18°$$

Thus for Fe··· ⇢ Fe·· at 18°

$$E_h = \varepsilon_{Fe^{\cdots} \to Fe^{\cdots}} - 0\cdot058 \log_{10} \frac{[Fe^{\cdot\cdot}]}{[Fe^{\cdots}]}.$$

Calculation shows that when all the iron is present as either ferrous or ferric ions, E_h in each case should be infinity. In actual fact, it is never quite possible to have the iron completely as ferrous or ferric ions, some exceedingly small amount of ferric or ferrous ions respectively always being present. For practical purposes, the potential corresponding to the beginning of the oxidation of $Fe^{..}$ to $Fe^{...}$ might be taken as that established when

$$\frac{[Fe^{..}]}{[Fe^{...}]} = \frac{99}{1},$$

i.e., E_h at beginning $= \varepsilon_{Fo^{...} \to Fo^{..}} - 2 \times 0.058$, whereas the potential when oxidation has been completed can be considered as that set up when

$$\frac{[Fe^{..}]}{[Fe^{...}]} = \frac{1}{99}$$

i.e., E_h at end $= \varepsilon_{Fc^{...} \to Fc^{..}} + 2 \times 0.058$.

At 50 per cent. oxidation $E_h = \varepsilon_{Fo^{...} \to Fo^{..}}$. The first part of the curve, given in Fig. 96, shows how E_h varies as ferrous ions are oxidised to ferric ions. It also shows that between 10 per cent. and 90 per cent. oxidation, a very gradual increase in E_h occurs. The increase is at a minimum at the middle of the oxidation. This curve is similar to that of the neutralisation of a weak acid or base in which buffer action on the *p*H is exhibited. The small change in E_h with the degree of oxidation (or reduction) from 10 per cent. to 90 per cent. oxidation (or reduction) is known as *poising action*.

Poising Action.

If α be taken as the fraction oxidised, then $1 - \alpha$ will be the fraction still in the reduced state. Then, taking the general case

$$E_h = \varepsilon_0 - \frac{RT}{(m-n)F} \log_e \frac{1-\alpha}{\alpha}$$

whence $$\frac{d\alpha}{dE_h} = \frac{(m-n)F}{RT}\alpha(1-\alpha).$$

Clark has suggested that $\dfrac{d\alpha}{dE_h}$ may be regarded as the *poising index*. With large values of $(m-n)$, the poising index is increased. Thus in the oxidation of stannous ions to stannic ions, $m-n = 2$, and consequently this system gives a poising action equal to double that of the ferrous-ferric system for the same degree of oxidation, α. Moreover, the E_h range within which oxidation (or reduction) occurs is much smaller. Thus the E_h at the beginning of oxidation is equal to

$$\varepsilon_{Sn^{...}\to Sn^{..}} - \frac{0.058}{2} \log \frac{99}{1} = \varepsilon_{Sn^{...}\to Sn^{..}} - 0.058 \; ;$$

at 50 per cent. oxidation, $E_h = \varepsilon_{Sn^{...}\to Sn^{..}}$ and at the end of oxidation

$$E_h = \varepsilon_{Sn^{...}\to Sn^{..}} - \frac{0.058}{2} \log \frac{1}{99} = \varepsilon_{Sn^{...}\to Sn^{..}} + 0.058.$$

Thus the change in E_h from 1 per cent. to 99 per cent. oxidation in the case of stannous ions is only 0.116 volt, compared with 0.232 volt in the case of ferrous ions.
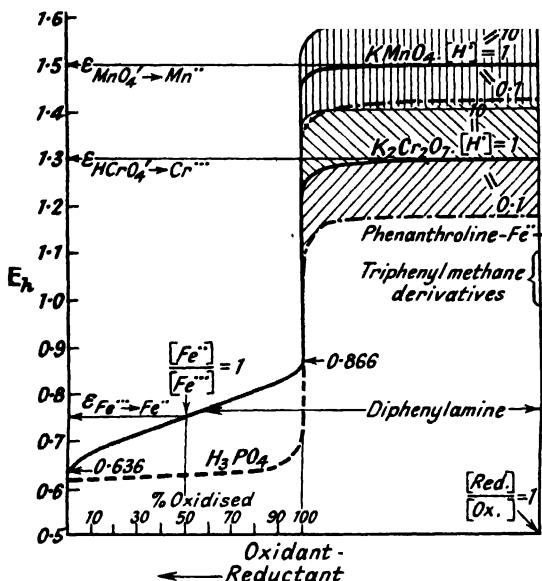
FIG. 96.—Potentiometric Titrations of (i) Fe$^{..}$ ions in Solutions of various Hydrogen-ion Concentrations with (a) KMnO$_4$, (b) K$_2$Cr$_2$O$_7$ (abscissæ reading from left to right), and (ii) (a) KMnO$_4$, (b) K$_2$Cr$_2$O$_7$ with Fe$^{..}$ ions (abscissæ reading from right to left).

Difficulties arise in measuring E_h for Sn$^{....}$ --> Sn$^{..}$, Cr$^{...}$ --> Cr$^{..}$ and Ti$^{....}$ --> Ti$^{...}$, on account of the very low values which are established and which therefore facilitate air-oxidation. In such cases, air should be rigidly excluded from the electrode vessel and an atmosphere of nitrogen should be maintained above the solution.

As stannous and stannic salts and titanous and titanic salts are considerably hydrolysed in solutions the respective ion concentrations cannot be taken as equal to the salt concentrations or to bear a comparable ratio to them in the reduced and oxidised

forms. More consistent values of E_h are obtained when sufficient acid has been inserted to repress hydrolysis. In dilute acid solutions the hydrogen-ion concentration has an appreciable effect on E_h. Thus Diethelm and Foerster (*Z. physikal. Chem.*, 1908, **62**, 138) found ε_0 for Ti'''' --> Ti''' in 4 N-H_2SO_4 to be $+ 0.120$ volt whereas it was $- 0.01$ in 0.4 N-H_2SO_4. Kolthoff (*Rec. trav. chim.*, 1924, **43**, 768) observed similar variations in hydrochloric acid solutions.

Case II

Systems involving Hydrogen Ions.

As examples we shall consider the two systems :

(*a*) $MnO_4' + 8H^{\cdot} \rightarrow Mn^{\cdot\cdot} + 4H_2O + 5F.E_{MnO_4' \rightarrow Mn^{\cdot\cdot}}$
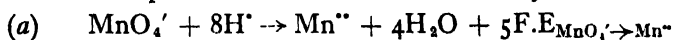
for which the effective oxidation intensity is given by

$$E_h = \varepsilon_{MnO_4' \rightarrow Mn^{\cdot\cdot}} - \frac{RT}{5F} \log_e \frac{[Mn^{\cdot\cdot}]}{[MnO_4'][H^{\cdot}]^8}$$

$$= \varepsilon_{MnO_4' \rightarrow Mn^{\cdot\cdot}} + \frac{8}{5} \cdot \frac{RT}{F} \log_e [H^{\cdot}] - \frac{RT}{5F} \log_e \frac{[Mn^{\cdot\cdot}]}{[MnO_4']}$$

(*b*) the redox system between quinquevalent and quadrivalent vanadium in acid solutions in which the ions concerned are respectively $VO_2^{\cdot}$ and $VO^{\cdot\cdot}$ Britton (*J. Chem. Soc.*, 1934, 1842 ; Britton and Welford, *ibid.*,   . The reaction is
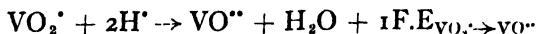
$$VO_2^{\cdot} + 2H^{\cdot} \rightarrow VO^{\cdot\cdot} + H_2O + 1F.E_{VO_2^{\cdot} \rightarrow VO^{\cdot\cdot}}$$

and

$$E_h = \varepsilon_{VO_2^{\cdot} \rightarrow VO^{\cdot\cdot}} - \frac{RT}{F} \log_e \frac{[VO^{\cdot\cdot}]}{[VO_2^{\cdot}][H^{\cdot}]^2}$$

$$= \varepsilon_{VO_2^{\cdot} \rightarrow VO^{\cdot\cdot}} + \frac{2RT}{F} \log_e [H^{\cdot}] - \frac{RT}{F} \log_e \frac{[VO^{\cdot\cdot}]}{[VO_2^{\cdot}]}.$$

In both the expressions for E_h, terms appear showing the importance which hydrogen ions have on the oxidation-reduction intensity. As a rule, those systems which are characterised by the more positive normal redox potentials, can effect the oxidation of systems having a lower normal redox potential, and the greater the difference between the normal redox potential of the oxidant and that of the reductant, the more completely will the reductant be oxidised. The precise criterion, however, is not the difference between the normal redox potentials but the actual differences that can be brought about between E_h for the two systems involved. The reverse is true in cases of reduction, the reducing agent having a lower E_h than that of the system undergoing reduction.

Fig. 96 illustrates (i) the oxidation of ferrous ions (as ferrous sulphate in sulphuric acid solution) with (*a*) potassium permanganate, (*b*) potassium dichromate, and (ii) the reduction of (*a*) potassium permanganate, (*b*) potassium dichromate, both in the presence of sulphuric acid, with ferrous ions (in ferrous sulphate)—in this case, the abscissæ reading in the reverse direction. During the first stage of the oxidation process the potential at the platinum electrode is governed entirely by the ratio of $Fe^{..}$ to $Fe^{...}$, the ions of the oxidising agent being without effect as the $MnO_4{}'$ (or $HCrO_4{}'$) ions are quantitatively reduced to $Mn^{..}$ (or $Cr^{...}$) ions. The ratio [Red]/[Ox] corresponding to the ions of the oxidising agent is thus equal to 100/o, which being indeterminate, cannot stabilise a potential at the platinum electrode. This state of affairs persists until the ferrous ions are almost completely converted into ferric ions, which, as shown in the previous paragraph, will occur when E_h has become

$$= \varepsilon_{Fe^{...} \to Fe^{..}} + 2 \times 0.058 = 0.75 + 0.116 = 0.866 \text{ volt.}$$

Immediately afterwards, a sudden increase in E_h occurs and as soon as unreduced $MnO_4{}'$ ions (or $HCrO_4{}'$) pass into solution, an equilibrium is established between them and $Mn^{..}$ (or $Cr^{...}$) formed in oxidising the $Fe^{..}$ ions. Using permanganate, the potentials then set up will be given at 18° by

$$E_h = 1.50 + \frac{8}{5} \times 0.058 \log_{10} [H^{.}] - \frac{0.058}{5} \log_{10} \frac{[Mn^{..}]}{[MnO_4{}']},$$

or if dichromate be employed by

$$E_h = 1.30 + \frac{7}{3} \times 0.058 \log_{10} [H^{.}] - \frac{0.058}{3} \log_{10} \frac{[Cr^{...}]}{[HCrO_4{}']}.$$

These expressions bring out clearly the considerable influence which hydrogen-ion concentration can have on E_h. The effects are illustrated in Fig. 97 in which curves indicate the variation in E_h when $[H^{.}] = \frac{1}{10}$, 1, and 10 g. ions/litre. The effect of low $[H^{.}]$ is to diminish the inflexion which marks the end-point, which incidentally tends to reduce the accuracy of potentiometric titration. In cases where E_h for the two stages lie closer together, a reduced $[H^{.}]$ may produce an indefinite inflexion resulting from incomplete oxidation when the equivalent amount of oxidising agent has been added. Similar considerations apply to the reduction titrations.

The potentiometric curves shown in Fig. 97 represent the variation in E_h during the progressive oxidation of vanadyl sulphate, $VOSO_4$, to $(VO_2)_2SO_4$ in the presence of different concentrations of sulphuric acid at 45° C. Curves A–F represent

titrations with 0·1 N-KMnO$_4$ of 100 c.c. of 0·00978 M.-VOSO$_4$ and x N-H$_2$SO$_4$ (A, x = 0·031 ; B, x = 0·071 ; C, x = 0·174 ; D, x = 0·398 ; E, x = 1·01 ; F, x = 1·81). Curves A′–F′ refer to the reductions with 0·1 N-FeSO$_4$ of solutions respectively represented by A–F, the reductions being commenced when the exact amounts of 0·1 N-KMnO$_4$ had been added to oxidise the vanadium completely to the quinquevalent state. These curves show how much the redox potential, E$_h$, of the system : 2H˙ + VO$_2$˙ → VO˙˙ + H$_2$O, depends on [H˙]. With increasing
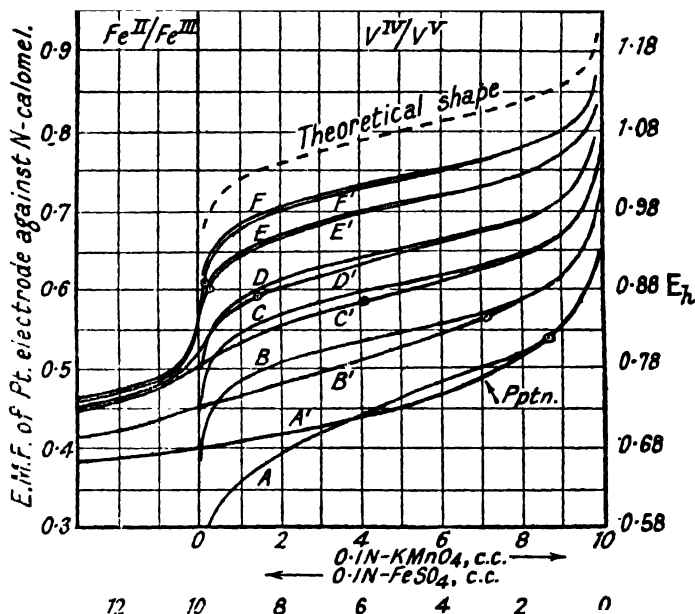
Fig. 97.—Potentiometric Titrations of : (1) solutions of Vanadyl Sulphate in the presence of various concentrations of Sulphuric Acid with Potassium Permanganate, and (2) Sulphuric Acid Solutions of Vanadium Pentoxide with Ferrous Sulphate at 45° C.

acid concentration the E$_h$ at the point of half-oxidation increases from + 0·747 (A), + 0·825 (B), + 0·886 (C), + 0·931 (D), + 997 (E) to + 1·02 (F). Incidentally, it becomes possible to reduce vanadium pentoxide in presence of much acid to the vanadyl state (Curves E′ and F′), the end-point being marked by a well-defined inflexion. This is not true in less acidic solutions (D′ and E′), whereas in very dilute acid solutions reduction is far from complete (Curves B′ and A′) ; in fact, ferric ions are then able to bring about a partial oxidation of quadrivalent

vanadium. This conclusion can be reached from a consideration of E_h corresponding to $Fe^{\cdots} \dashrightarrow Fe^{\cdots}$, which at $45°$ is given by

$$E_h = 0.75 - 0.063 \log_{10} \frac{[Fe^{\cdots}]}{[Fe^{\cdots}]}$$

in conjunction with E_h values indicated by either A or B. Another point is that, owing to the high E_h, vanadyl sulphate is stable in solution in the presence of much sulphuric acid, whereas it undergoes air-oxidation when the concentration of sulphuric acid is low.

Except in the presence of the lowest concentration of sulphuric acid (Curve A), the oxidation of the vanadyl sulphate follows the equation :

$$H_2O + VO^{\cdots} \dashrightarrow 2H^{\cdot} + VO_2^{\cdot}$$
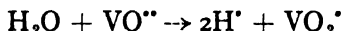
so that as the oxidation proceeds at $45°$

$$E_h = \varepsilon_{VO_2^{\cdot} \rightarrow VO^{\cdots}} + 2 \times 0.063 \log_{10} [H^{\cdot}] - 0.063 \log_{10} \frac{[VO^{\cdots}]}{[VO_2^{\cdot}]}.$$

The broken curve, marked " Theoretical shape," gives the form of the curve which would result, if $[H^{\cdot}]$ for any given titration remained constant, and the variation in E_h depended only on the ratio $[VO^{\cdots}]/[VO_2^{\cdot}]$, i.e., [Red]/[Ox], which appears in the third term. Actually, as the oxidation continues there is a gradual withdrawal of hydrogen ions from the solution as indicated by the ionic equation :

$$MnO_4{'} + VO^{\cdots} + 6H^{\cdot} \dashrightarrow Mn^{\cdots} + VO_2^{\cdot} + 3H_2O.$$
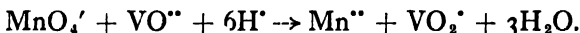
Provided that the concentration of sulphuric acid is relatively large compared with that of the vanadyl sulphate, these changes in $[H^{\cdot}]$ will be relatively small, and will not greatly influence E_h as shown by the uppermost curves F, E, D. The departure of the lower curves C, B, A, from the " theoretical shape " is attributable to the gradually diminishing hydrogen-ion concentration as the titration proceeds. Another factor arises in the case of titration A, viz., that owing to the relatively low concentration of sulphuric acid there is a possibility of some of the vanadium pentoxide, which is formed, being present in the form of polyvanadate anions and not as $VO_2^{\cdot}$ cations.

The dependence of the system, $V^{IV} \dashrightarrow V^V$, on $[H^{\cdot}]$ is seen from the measurements of E_h by Britton and Welford (J. Chem. Soc., 1942), on solutions, 0.05 M. with respect to vanadium, one-half being present as $VOCl_2$ and the other as VO_2Cl, together with varying amounts of free hydrochloric acid.

TABLE 157

E_h AND $\varepsilon_{VO_2^+ \to VO^{..}}$ AT 25°

N-HCl.	E_h.	ε.
0·093	+ 0·876	+ 1·003
0·143	+ 0·903	+ 1·008
0·321	+ 0·941	+ 1·007
0·510	+ 0·964	+ 1·008
0·690	+ 0·981	+ 1·010

Table 157 shows that although E_h changes in hydrochloric acid solution materially with [H'], the normal " redox " potential, ε, remains sensibly constant. For the purpose of computing [H'] the degrees of ionisation as given by conductivity data were employed, although if the mean activities a_+ be used instead and the activities of the VO'' and VO$_2$' ions be assumed equal to their concentrations, reasonably constant values of ε are obtained.

The titration curves in Fig. 98, which are those obtained by Lingane and Karplus (*Anal. Chem.*, 1946, **18**, 191) illustrate
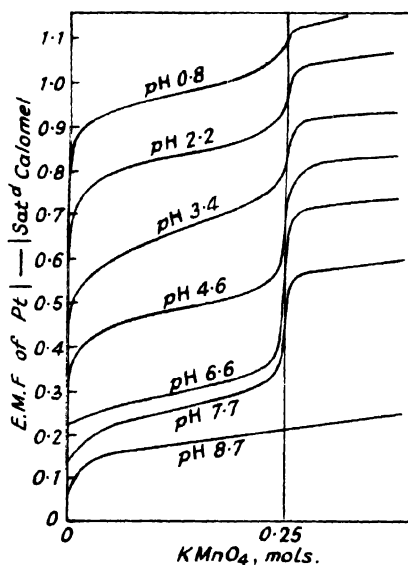
FIG. 98.

J J. Lingane and R. Karplus, *Anal. Chem.*,
1946, **18**, 192

the potential of a platinum electrode in solutions, having the same concentrations of manganous ions and pyrophosphoric acid but which were buffered at different pH values, as the manganous ions were oxidised to the manganic state by the progressive addition of potassium permanganate. It will be observed that the effect of raising the pH was to cause the potentials to become smaller not only during the actual oxidation but after it had been completed. As the potentials before and after the end-point did not change to the same extent the magnitude of the inflexions increased as the pH was raised from 0·3 to 6·6.

Expressed ionically the oxidation was :

$$MnO_4{'} + 4Mn^{..} + 8H^{.} \rightarrow 5Mn^{...} + 4H_2O.$$

During the oxidation process, which was

$$Mn^{..} + F \rightarrow Mn^{...},$$

the potential of the platinum electrode,

$$E_{Pt} = \varepsilon_{0_{Mn^{...} \rightarrow Mn^{..}}} - \frac{RT}{F} \log_e \frac{[Mn^{..}]}{[Mn^{...}]},$$

whereas afterwards, the potential of the platinum electrode was determined by the system :

$$MnO_4{'} + 8H^{.} \rightarrow Mn^{...} + 4H_2O + 4F,$$

thus $$E_{Pt} = \varepsilon_{0_{MnO_4{'} \rightarrow Mn^{...}}} - \frac{RT}{4F} \log_e \frac{[Mn^{...}]}{[MnO_4{'}][H^{.}]^8}.$$

It is probable that the difference in the final potentials set up in the various titrations can be largely accounted for by the substantial difference in hydrogen ion activity, i.e. by the term $[H^{.}]^8$ in the foregoing equation. During the oxidation reaction the potential should be independent of hydrogen ion activity and depend on $[Mn^{..}]$ and $[Mn^{...}]$. The curves clearly show, however, that pH was playing an important role and it would appear that in so doing the $[Mn^{...}]$ was being reduced, thus increasing the ratio $\dfrac{[Mn^{..}]}{[Mn^{...}]}$,

with the consequent effect of reducing E_{Pt}.

In view of the dissociation constants of $H_4P_2O_7$ being $K_{a_1} = 1\cdot4 \times 10^{-1}$, $K_{a_2} = 1\cdot1 \times 10^{-2}$, $K_{a_3} = 2\cdot1 \times 10^{-7}$ and $K_{a_4} = 4 \times 10^{-10}$ and the effect of pH being greatest in the

solution buffered at pH 6·6, it is highly feasible that the manganic ions were removed from the sphere of action as a complex in which the second stage of dissociation of pyrophosphoric acid was involved. Evidence was advanced by Waters and Kolthoff (*Ind. Eng. Chem., Anal. Edn.*, 1943, **15**, 8; 1944, **16**, 187) for the existence of the anion $Mn(H_2P_2O_7)_3'''$ between pH 2 and pH 5, and it is highly probable that the anions were formed in the course of the first four titrations.

Case III

Systems involving the Oxidation and Reduction of Organic Bodies in which Hydrogen Ions are indirectly involved.

These systems have already been discussed. Many of the dyestuffs, which have been proposed as redox indicators, undergo reduction at potentials, E_h, governed by the expression:

$$E_h = \varepsilon' - \frac{RT}{nF} \log_e \frac{[Red]}{[Ox]} + \phi[H^{\cdot}],$$

in which n is the valency change and $\phi[H]$ a function of the hydrogen-ion concentration and the dissociation constants of the ionisations that may occur. Usually $n = 2$. Hence at a fixed pH, $\phi[H] = \beta$, a constant, and

$$E_h = \varepsilon' + \beta - \frac{RT}{2F} \log_e \frac{[Red]}{[Ox]}$$

$$= \varepsilon'' - 0.000{,}099{,}2\,T\log_{10} \frac{[\text{Intensity of Colour of Reduced Form}]}{[\text{Intensity of Colour caused by unreduced Dye}]}$$

$$[\varepsilon'' \text{ being equal to } \varepsilon' + \beta),$$

$$= \varepsilon'' - 0.030 \log_{10} \frac{x}{100 - x} \text{ at } 30°$$

and

$$E_h = \varepsilon'' - 0.029 \log_{10} \frac{x}{100 - x} \text{ at } 18°,$$

the potential of a platinum electrode in solutions, having the same concentrations of manganous ions and pyrophosphoric acid but which were buffered at different pH values, as the manganous ions were oxidised to the manganic state by the progressive addition of potassium permanganate. It will be observed that the effect of raising the pH was to cause the potentials to become smaller not only during the actual oxidation but after it had been completed. As the potentials before and after the end-point did not change to the same extent the magnitude of the inflexions increased as the pH was raised from 0·3 to 6·6.

Expressed ionically the oxidation was :

$$\text{MnO}_4{}' + 4\text{Mn}{}^{\cdot\cdot} + 8\text{H}{}^{\cdot} \rightarrow 5\text{Mn}{}^{\cdot\cdot\cdot} + 4\text{H}_2\text{O}.$$

During the oxidation process, which was

$$\text{Mn}{}^{\cdot\cdot} + \text{F} \rightarrow \text{Mn}{}^{\cdot\cdot\cdot},$$

the potential of the platinum electrode,

$$\text{E}_{\text{Pt}} = \varepsilon_{0_{\text{Mn}{}^{\cdot\cdot\cdot}\rightarrow\text{Mn}{}^{\cdot\cdot}}} - \frac{\text{RT}}{\text{F}} \log_e \frac{[\text{Mn}{}^{\cdot\cdot}]}{[\text{Mn}{}^{\cdot\cdot\cdot}]},$$

whereas afterwards, the potential of the platinum electrode was determined by the system :

$$\text{MnO}_4{}' + 8\text{H}{}^{\cdot} \rightarrow \text{Mn}{}^{\cdot\cdot\cdot} + 4\text{H}_2\text{O} + 4\text{F},$$

thus $$\text{E}_{\text{Pt}} = \varepsilon_{0_{\text{MnO}_4{}'\rightarrow\text{Mn}{}^{\cdot\cdot\cdot}}} - \frac{\text{RT}}{4\text{F}} \log_e \frac{[\text{Mn}{}^{\cdot\cdot\cdot}]}{[\text{MnO}_4{}'][\text{H}{}^{\cdot}]^8}.$$

It is probable that the difference in the final potentials set up in the various titrations can be largely accounted for by the substantial difference in hydrogen ion activity, i.e. by the term $[\text{H}{}^{\cdot}]^8$ in the foregoing equation. During the oxidation reaction the potential should be independent of hydrogen ion activity and depend on $[\text{Mn}{}^{\cdot\cdot}]$ and $[\text{Mn}{}^{\cdot\cdot\cdot}]$. The curves clearly show, however, that pH was playing an important role and it would appear that in so doing the $[\text{Mn}{}^{\cdot\cdot\cdot}]$ was being reduced, thus increasing the ratio $\dfrac{[\text{Mn}{}^{\cdot\cdot}]}{[\text{Mn}{}^{\cdot\cdot\cdot}]}$,

with the consequent effect of reducing E_{Pt}.

In view of the dissociation constants of $\text{H}_4\text{P}_2\text{O}_7$ being $\text{K}_{a_1} = 1\cdot4 \times 10^{-1}$, $\text{K}_{a_2} = 1\cdot1 \times 10^{-2}$, $\text{K}_{a_3} = 2\cdot1 \times 10^{-7}$ and $\text{K}_{a_4} = 4 \times 10^{-10}$ and the effect of pH being greatest in the

solution buffered at pH 6·6, it is highly feasible that the manganic ions were removed from the sphere of action as a complex in which the second stage of dissociation of pyrophosphoric acid was involved. Evidence was advanced by Waters and Kolthoff (*Ind. Eng. Chem., Anal. Edn.*, 1943, **15**, 8 ; 1944, **16**, 187) for the existence of the anion $Mn(H_2P_2O_7)_3'''$ between pH 2 and pH 5, and it is highly probable that the anions were formed in the course of the first four titrations.

Case III

Systems involving the Oxidation and Reduction of Organic Bodies in which Hydrogen Ions are indirectly involved.

These systems have already been discussed. Many of the dyestuffs, which have been proposed as redox indicators, undergo reduction at potentials, E_h, governed by the expression :

$$E_h = \varepsilon' - \frac{RT}{nF} \log_e \frac{[Red]}{[Ox]} + \phi[H^{\cdot}],$$

in which n is the valency change and $\phi[H]$ a function of the hydrogen-ion concentration and the dissociation constants of the ionisations that may occur. Usually $n = 2$. Hence at a fixed pH, $\phi[H] = \beta$, a constant, and

$$E_h = \varepsilon' + \beta - \frac{RT}{2F} \log_e \frac{[Red]}{[Ox]}$$

$$= \varepsilon'' - 0\cdot000,099,2 T \log_{10} \frac{[\text{Intensity of Colour of Reduced Form}]}{[\text{Intensity of Colour caused by un-}}$$
$$\text{reduced Dye}]$$

$$[\varepsilon'' \text{ being equal to } \varepsilon' + \beta),$$

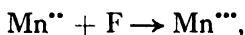$$= \varepsilon'' - 0\cdot030 \log_{10} \frac{x}{100 - x} \text{ at } 30°$$

and

$$E_h = \varepsilon'' - 0\cdot029 \log_{10} \frac{x}{100 - x} \text{ at } 18°,$$

where x = percentage of indicator reduced and $\therefore$ 100 $- x$ = percentage of indicator not reduced. We can consider reduction effectively to begin when $x = 1$ and to end when $x = 99$, whence it follows that the E_h range within which colour changes occur will be given by

$$E_h = \varepsilon'' \pm 2 \times 0 \cdot 030 \text{ at } 30°$$

and $\qquad E_h = \varepsilon'' \pm 2 \times 0 \cdot 029 \text{ at } 18°.$

The full range over which a redox indicator can be used is 0·120 volt at 30° and 0·116 volt at 18°. When $x = 50$ per cent., $E_h = \varepsilon''$.

Such changes are illustrated in Fig. 99 which refers to the reduction of the indigo sulphonates at pH 3·91 at 30° (Sullivan, Cohen and Clark, *loc. cit.*). Actually, the range over · which an indicator can be used is somewhat smaller, owing to the difficulty of the eye to perceive slight differences which occur when the indicator begins to be reduced, extending to a point when $x =$ about 15. In Fig. 99 the values of E_h corresponding to half-reduction are those of ε'' for pH 3·91. Table 158 gives the values of ε'' at pH 7 for a number of redox indicators, whereas Table 159. records the values corresponding to pH values ranging from 5·0 to 9·0. This table was compiled by Clark *et al.* (*U.S. Hyg. Lab. Bull.* No. 151, 1928), see also

Fig. 99.—Showing the Dependence on E_h of the Oxidation and Reduction of Indigo Sulphonates at a fixed pH, 3·91, at 30°.

Hewitt (*Oxidation-Reduction Potentials in Bacteriology and Biochemistry*, L.C.C., 1937).

TABLE 158

$\varepsilon_h{}''$ AT pH 7 OF REDOX INDICATORS OR E_h AT HALF-REDUCTION

	$= \varepsilon_h{}''.$	rH.
Diphenylamine sulphonic acid	—	26–28
Phenol-m-sulphonate-indo-2 : 6-dibromophenol	+ 0·273	—
m-Chlorophenol-indo-2 : 6-dichlorophenol . .	+ 0·254	—
m-Bromophenol indophenol	+ 0·248	—
Phenol-o-sulphonate-indo-2 : 6-dibromophenol	+ 0·242	—
o-Chlorophenol indophenol	+ 0·233	20–22
o-Bromophenol indophenol	+ 0·230	20–22
Phenol indophenol	+ 0·227	20–22
Bindscheldler's green (C.I. 819)	+ 0·224	20–22
Phenol Blue.	+ 0·224	20–22
2 : 6-Dichlorophenol indo-o-chlorophenol . .	+ 0·219	20–22
2 : 6-Dibromophenol indophenol.	+ 0·218	20–22
2 : 6-Dichlorophenol indophenol	+ 0·217	20–22
m-Cresol indophenol	+ 0·208	19–21
o-Cresol indophenol	+ 0·191	18·5–20·5
2 : 6-Dichlorophenol indo-o-cresol	+ 0·181	18–20
Thymol indophenol	+ 0·174	18–20
2 : 6-Dibromophenol indo-guaiacol	+ 0·159	17·5–19·5
m-Toluylenediamine indophenol	+ 0·125	16·5–18·5
1-Naphthol-2-sodium sulphonate indophenol .	+ 0·123	16·5–18·5
1-Naphthol-2-sodium sulphonate-indo-2 : 6-dichlorophenol	+ 0·119	16–18
Toluylene Blue.	+ 0·115	16–18
Thionine (Lauth's violet, C.I. 920) . . .	+ 0·063	15–17
Prune	+ 0·056	15–17
Cresyl Blue, or Brilliant Blue (C.I. 877 , S. 621)	+ 0·047	15–17
Gallocyanine	+ 0·021	—
Methylene Blue (C.I. 922 ; S. 659) . . .	+ 0·010	—
Ciba Scarlet sulphonate	− 0·036	—
Indigo tetrasulphonate of potassium . . .	− 0·046	11–13
Methyl Capri Blue	− 0·060	—
Indigo trisulphonate of potassium	− 0·081	9·5–11·5
Indigo disulphonate of potassium	− 0·125	8–10
Gallophenine	− 0·142	—
Brilliant Alizarine Blue	− 0·173	—
2-Methyl-3-hydroxy-1 : 4-naphthoquinone (phthiocol)	− 0·180	—
Phenosafranine, Safranine B (C.I. 840) . .	− 0·252	5–7
Tetraethyl phenosafranine chloride ; Iris Violet (C.I. 847 ; S. 686)	− 0·252	5–7
Dimethylphenosafranine, Fuchsia, Methylene Violet BN (C.I. 842 ; S. 680)	− 0·260	—
Tetramethyl phenosafranine	− 0·273	—
Safranine-T (C.I. 841 ; S. 679)	− 0·290	4–7
Induline Scarlet	− 0·299	—
Neutral Red (C.I. 825 ; S. 670)	− 0·325	—
Rosindone sulphonate, No. 6	− 0·385	—
Viologens	− 0·400	—

TABLE 159

ε_h Potentials at Various pH Values at 30° of "Redox" Indicators

pH.	Indigo disulphonate.	Indigo trisulphonate.	Indigo tetrasulphonate.	Methylene Blue.	Thionine.	1-Naphthol-2-sodium sulphonate 2:6-dichlorophenol.	1-Naphthol 2-sodium sulphonate indophenol.	Toluylene Blue.	Thymol indophenol.	2:6 Dichlorophenol indo-o-cresol.	o-Cresol indophenol.	m-Cresol indophenol.	2:6 Dibromophenol indophenol.	2:6 Dichlorophenol indophenol.	o-Bromophenol indophenol.	Phenol indophenol.	o-Chlorophenol indophenol.	m-Chlorophenol indo-2:6 dichlorophenol.	Phenol-m-sulphonate indo-2:6 dibromophenol.
5.0	−0.010	+0.032	+0.065	+0.101	+0.138	+0.262		+0.221		+0.335				+0.366				+0.391	+0.390
5.2	−0.022	+0.020	+0.053	+0.088	+0.124	+0.249		+0.208		+0.322				+0.352				+0.378	+0.378
5.4	−0.034	+0.008	+0.041	+0.077	+0.112	+0.236		+0.196		+0.307				+0.339				+0.366	+0.366
5.6	−0.045	−0.004	+0.029	+0.066	+0.106	+0.223		+0.184		+0.292				+0.325				+0.351	+0.354
5.8	−0.057	−0.016	+0.017	+0.056	+0.100	+0.210		+0.173	+0.244	+0.277				+0.310	+0.308			+0.339	+0.342
6.0	−0.069	−0.028	+0.006	+0.047	+0.094	+0.196	+0.183	+0.162	+0.233	+0.261	+0.243			+0.295	+0.296		+0.301	+0.326	+0.330
6.2	−0.081	−0.039	−0.006	+0.039	+0.087	+0.181	+0.171	+0.151	+0.222	+0.245	+0.230	+0.259		+0.279	+0.284	+0.276	+0.288	+0.312	+0.319
6.4	−0.092	−0.051	−0.017	+0.031	+0.080	+0.166	+0.159	+0.141	+0.211	+0.228	+0.217	+0.246		+0.263	+0.272	+0.265	+0.275	+0.297	+0.307
6.6	−0.104	−0.061	−0.027	+0.024	+0.074	+0.150	+0.147	+0.132	+0.198	+0.212	+0.204	+0.233		+0.247	+0.259	+0.254	+0.262	+0.282	+0.295
6.8	−0.114	−0.072	−0.037	+0.017	+0.068	+0.134	+0.135	+0.123	+0.185	+0.196	+0.191	+0.221		+0.232	+0.245	+0.241	+0.248	+0.268	+0.284
7.0	−0.125	−0.081	−0.046	+0.011	+0.062	+0.119	+0.123	+0.115	+0.174	+0.181	+0.180	+0.208	+0.218	+0.217	+0.230	+0.227	+0.233	+0.254	+0.273
7.2	−0.134	−0.091	−0.055	+0.004	+0.056	+0.103	+0.111	+0.108	+0.160	+0.166	+0.168	+0.197	+0.204	+0.203	+0.215	+0.212	+0.218	+0.240	+0.262
7.4	−0.143	−0.099	−0.062	−0.002	+0.050	+0.088	+0.099	+0.101	+0.148	+0.152	+0.156	+0.185	+0.190	+0.189	+0.200	+0.200	+0.203	+0.226	+0.251
7.6	−0.152	−0.107	−0.070	−0.008	+0.043	+0.073	+0.088	+0.094	+0.136	+0.138	+0.143	+0.173	+0.176	+0.175	+0.184	+0.186	+0.187	+0.213	+0.240
7.8	−0.160	−0.114	−0.077	−0.014	+0.037	+0.060	+0.074	+0.088	+0.123	+0.125	+0.130	+0.160	+0.163	+0.162	+0.167	+0.170	+0.170	+0.200	+0.229
8.0	−0.167	−0.121	−0.083	−0.020	+0.030	+0.046	+0.062	+0.082	+0.110	+0.112	+0.116	+0.148	+0.151	+0.150	+0.152	+0.155	+0.155	+0.188	+0.218
8.2	−0.174	−0.127	−0.090	−0.026	+0.025	+0.034	+0.049	+0.075	+0.097	+0.099	+0.102	+0.134	+0.138	+0.137	+0.137	+0.139	+0.139	+0.176	+0.207
8.4	−0.180	−0.134	−0.096	−0.032	+0.020	+0.021	+0.026	+0.069	+0.084	+0.087	+0.086	+0.120	+0.126	+0.125	+0.120	+0.124	+0.124	+0.164	+0.197
8.6	−0.187	−0.140	−0.102	−0.038	+0.014	+0.002	+0.023	+0.063	+0.069	+0.075	+0.076	+0.105	+0.114	+0.113	+0.105	+0.110	+0.109	+0.153	+0.187
8.8	−0.193	−0.146	−0.108	−0.044	+0.008	−0.002	+0.010	+0.057	+0.056	+0.063	+0.057	+0.091	+0.102	+0.101	+0.092	+0.096	+0.095	+0.143	+0.177
9.0	−0.199	−0.152	−0.114	−0.050	−0.001	−0.012	−0.003	+0.051	+0.041	+0.051		+0.076	+0.090	+0.089	+0.079	+0.083	+0.082	+0.133	+0.168

Colorimetric Estimation of E_h.

Redox indicators may be used by employing the foregoing principles to measure the E_h of a system at a given pH.   Colours corresponding to the range of usefulness of the indicator may be obtained by adding definite amounts of dye solution to solutions buffered at the same pH and containing a suitable redox system which " poises " the solution at some precise E_h.   The test solution, which should be of the same volume as that of the " poised " standards, should be treated with the correct volume of indicator.   The colour produced in the test solution can then be compared with the standards.   It is advisable to prepare standards immediately before use.

Colorimetric methods, similar to those of Gillespie for the determination of pH, page 394, Vol. I, may be used, with the exception that suitable oxidising and reducing agents must be employed to develop the respective full colours of the oxidised and reduced forms.

The majority of dyes used as " redox " indicators yield colourless solutions on reduction, but mention should be made of the " viologens " (N.N'-disubstituted-4 : 4'-dipyrylidinium chlorides, Michaelis, *Biochem. Z.*, 1932, **250**, 564 ;   Michaelis and Hill, *J. Amer. Chem. Soc.*, 1933, **55**, 1481) which are coloured in the reduced state.

The Term rH.

It was shown on pages 18, Vol. I and 60, Vol. I that the potential of a hydrogen electrode depends, not only on the hydrogen-ion concentration of the solution in which it is immersed, but on the pressure, π, of hydrogen gas surrounding the electrode.   The potential may therefore be represented :

$$E_{H_{,\pi}} = \frac{2 \cdot 3026 RT}{2F} \cdot (r\mathrm{H} - 2p\mathrm{H})$$

where rH is a symbol, introduced by Clark (*U.S. Hyg. Lab. Bull.* No. 151, 1928, page 27), to represent $-\log_{10} \pi$ or $\log_{10} \frac{1}{\pi}$, π being in atmospheres pressure.

Incidentally, the above expression gives $E_{H_{,\pi}}$ in terms of the arbitrary hydrogen electrode, for when $\pi = 1$ atmos. and $[H^{\cdot}] = 1$, rH $= 0$ and pH $= 0$, whence

$$E_{H_{,\pi = 1, \, [H^{\cdot}] = 1}} = 0.$$

Although $E_h = \varepsilon_{\mathrm{Ox} \to \mathrm{Red}} - \dfrac{RT}{nF} \log_e \dfrac{[\mathrm{Red}]}{[\mathrm{Ox}]}$

gives the potential set up at an inert electrode, such as platinum, by a " redox " system, Clark considered that the redox potential, E_h, might also be regarded as that of a hypothetical hydrogen electrode supplied with gaseous hydrogen at π atmospheres. At any given pH, π would therefore give a measure of the " redox " intensity, or, as stated by Clark, this hypothetical pressure, π, can be more conveniently expressed by the term rH ; π being equal to 10^{-rH}

$$E_h - E_{H_2\pi} = 0\cdot0000992T \cdot rH - 0\cdot0001984T \cdot pH,$$

and substituting the pH value of the solution containing the " redox " system, it is possible to calculate rH. For example, if we consider the system $Fe^{\cdots} \to Fe^{\cdots}$ in hydrochloric acid solution, E_h at half-reduction $= \varepsilon_{Fe^{\cdots} \to Fe^{\cdots}} = + 0\cdot75$ volt, a value which is nearly independent of $[H^{\cdot}]$, except when the concentration of free acid is very low and is insufficient to repress the hydrolysis of the ferric salt. This will tend to diminish $[Fe^{\cdots}]$.

If $[H^{\cdot}] = 1$, $i.e.$, $pH = 0$, then at 18°, $rH = \dfrac{0\cdot75}{0\cdot029} = 26$, whereas, if $[H^{\cdot}] = 5$ gm. hydrogen-ions/litre, $i.e.$, $pH = -0\cdot70$, and therefore

$$rH = \frac{0\cdot75 - 0\cdot058 \times 0\cdot70}{0\cdot029} = 24.$$

These rH values indicate that hydrogen electrodes which would reach the potential of $+ 0\cdot75$ volt would have to be supplied with hydrogen gas at the respective pressures of 10^{-26} and 10^{-24} atmospheres. Such pressures are impracticable, but still the rH values might be considered as an alternative method of expressing the oxidising tendency ; the higher the rH value the greater the oxidising intensity, whilst systems of low rH have a high reducing intensity. The higher rH value, 26, for $Fe^{\cdots} \to Fe^{\cdots}$, when $[H^{\cdot}] = 1$, than that indicated when $[H^{\cdot}] = 5$, $viz.$, 24, would suggest that ferric ions possess slightly greater oxidising intensity in dilute acid than in concentrated acid solutions. This is not the case. This constitutes a serious objection to the application of rH to redox systems which are not affected by hydrogen ions.

Regarding organic redox systems, we have seen that E_h can generally be represented by

$$E_h = \varepsilon' - 2\cdot3026\frac{RT}{2F} \log_{10} \frac{[Red]}{[Ox]} + \phi[H^{\cdot}].$$

If we attempt to consider these systems in terms of the hypothetical hydrogen electrode, then as $E_h = E_{H_2\pi}$, it follows that

$$\epsilon' - 2 \cdot 3026 \frac{RT}{2F} \log_{10} \frac{[Red]}{[Ox]} + \phi[H^\cdot] = \frac{2 \cdot 3026 \, RT}{2F} . \, rH - 2 \cdot 3026 \frac{RT}{F} pH.$$

If
$$\phi[H^\cdot] = - 2 \cdot 3026 \frac{RT}{F} . \, pH$$

then
$$\epsilon' - \frac{2 \cdot 3026 RT}{2F} \log_{10} \frac{[Red]}{[Ox]} = \frac{2 \cdot 3026 RT}{2F} . \, rH$$

and when
$$[Red] = [Ox],$$

$$\epsilon' = \frac{2 \cdot 3026 RT}{2F} . \, rH.$$

When such conditions are satisfied, then both ϵ' and rII afford a measure of the redox intensity which is independent of the pH of the redox solution. As the term $- 2 \cdot 3026 \frac{RT}{F} . \, pH$ gives the potential of the ordinary hydrogen electrode ($\pi = 1$ atmos.) in the particular solution, it is seen that ϵ' gives the potential of the inert electrode referred to that of this hydrogen electrode, and therefore when the conditions exist that render

$$\epsilon' = \frac{2 \cdot 3026 RT}{2F} . \, rH,$$

then the values of rH so calculated, as indeed do those of ϵ', provide a true measure of the redox intensity which is independent of pH. The necessary condition for this to occur is

$$\phi[H^\cdot] = - 2 \cdot 3026 \frac{RT}{F} . \, pH,$$

and this is true only of systems of the type : Ox $\rightarrow$ Red" when the terms, $K_1[H^\cdot]$ and K_1K_2, in the complete expression (p. 3) can be ignored. As Fig. 94 shows, this state of affairs is true of the systems there represented for pH values below 7. The E_h/pH curves are then parallel to the curve indicating the potentials of the hydrogen electrode. The difference between E_h and E_{II}, at any pH value is clearly equal to ϵ' of the " redox " system in question. No such regularity holds when the terms $K_1[H^\cdot]$ and K_1K_2 become operative. There is also no such regularity to be observed in the more complicated systems to which Fig. 95 refers, and no advantages can accrue from the use of rH ; in fact, Clark has himself suggested that the use of the term, should be discontinued. It may, of course, be employed if the precise pH at which the E_h measurement is made, is mentioned. Thus the rH values given in Table 158 refer to computations based on E_h data at pH 7. It seems more desirable to record the actual

E_h measurement at a specified pH value. In spite of such objections to the use of rH, it would appear from its frequent application to industrial and biochemical oxidation-reduction systems that the term has come to stay.

Use of Redox Indicators in Volumetric Analysis.

In order to understand fully the ability of a " redox " indicator to indicate the attainment of the end-point in an oxidation- or reduction-titration, it is essential to ascertain the nature and magnitude of the inflexion in the E_h/titrant curve at that stage, and then to select the potential, E_h, which corresponds exactly, or, as nearly as possible, with the addition of the stoicheiometric volume of titrant. As already shown in this chapter, the ε_h'' of many " redox " indicators is determined by the pH of the solution during titration. In addition to the redox indicators already mentioned, a number of other " redox " indicators have been described, and although their E_h characteristics have not been thoroughly investigated, they have been found experimentally to indicate correct end-points. Table 160 gives a number of indicators, together with their approximate transition potentials, in terms of E_h, at which they visually undergo change in colour in titrimetric work as determined during redox potentiometric titrations.

TABLE 160

Indicator.	E_h
Ferrous o-phenanthroline sulphate	+ 1·14
Xylene Blue VS	+ 1·093
N-Phenylanthranilic acid (o-diphenylamine carboxylic acid)	+ 1·08
Setopalin	+ 1·063
Cyanol fast Green 2G	+ 1·033
Xylene Blue AS	+ 1·023
Acronol Brilliant Blue BDC	+ 1·013
Cyanin B	+ 1·013
Eriogreen B	+ 1·013
Setoglaucin O	+ 1·003
Xylene Cyanole FF	+ 0·993
Patent Blue A	+ 0·993
Erioglaucin A	+ 0·993
Diphenylbenzidine	+ 0·83
Diphenylamine	+ 0·76
Diphenylamine sulphonic acid	+ 0·76
Methyl Red	ca + 0·8
Alphazurine G (Neptune Blue BG)	?
Methyl Orange	?

Excepting the indicators given at the bottom of Table 160, all the indicators change in colour at about $E_h = 1$ volt. They are therefore of service in detecting the end-points in titrations with strong oxidising agents such as ceric sulphate and potassium

permanganate. Unfortunately, few indicators which refer to low E_h values are yet available, the notable indicator of this type being methylene blue. Titrations involving such a strong reducing agent as trivalent titanium ions may therefore be performed with the aid of methylene blue see Knecht and Hibbert, (" New Reduction Methods of Volumetric Analysis," London, 1925). In preparing solutions of many " redox " indicators sulphuric or hydrochloric acid must be included. Difficulties encountered in the use of " redox " indicators lie in their colour changes either being sluggish or irreversible and sometimes both. An irreversible colour change restricts the use of the indicator in titrations to one direction only, the titrant being the oxidising agent or else the reducing agent. This precludes the possibility of back-titrating, especially when once the end-point has been overrun. There is also with many of the indicators a distinct tendency for them to be adsorbed by one of the reactants, and to minimise errors they must be introduced very shortly before reaching the end-point. A few typical examples of the application of " redox " indicators to actual titrations will now be given.

(i) **Methylene Blue.**
Methylene blue is interesting in that it is occasionally used for the dual purpose of oxidising agent and indicator, and sometimes only as " redox " indicator. Furthermore, its " redox " potential, E_h, as Fig. 95 shows, depends largely on pII.

(a) *As Oxidant and Indicator.*
Hibbert (*J. Soc. Chem. Ind.*, 1909, **48**, 189T) showed that hydrochloric acid solutions of titanous chloride can be accurately titrated with a solution of methylene blue. As long as Ti···· ions remain, the methylene blue will be decolorised, the end-point being marked by the deep blue colour imparted to the solution by the first drop of methylene blue added in excess. Moreover, the method is applicable in the presence of ferrous ions as they are unable to reduce methylene blue.

The reason why such a method is possible is forthcoming from a study of the redox potentials involved. The normal oxidation-reduction potential of Ti···· → Ti··· is + 0·06, which means that at E_h = + 0·06 + 0·116 = + 0·18 the oxidation of titanous ions to titanic ions is, in effect, complete (actually [Ti····]/[Ti···] = 99/1). Fig. 95 shows that in strongly acid solution methylene blue is half-reduced at E_h = + 0·53, whilst calculation reveals that oxidation of methylene blue just begins at E_h = + 0·47 and ends at E_h = + 0·59. These potentials,

compared with those characteristic of the titanous-titanic system, indicate that methylene blue is an effective oxidant of titanous ions. After oxidation is complete, the excess methylene blue will establish an E_h ranging between $+ 0.47$ and $+ 0.53$, the latter value being reached only when a very considerable excess of oxidant has been added. On the other hand, $\varepsilon_{0_{Fe^{...}\rightarrow Fe^{..}}} = + 0.75$, whence the redox range lies between $+ 0.634$ and $+ 0.866$ at 18° C. A potential so high as $+ 0.626$ cannot be reached by the methylene blue system and consequently ferrous ions are unaffected by methylene blue.

Another instructive example is that of the volumetric titration of molybdic acid, or of the ammonium phospho-molybdate precipitate. After dissolution in concentrated acid, the molybdenum is reduced with zinc in an air-free atmosphere to the tervalent state and after boiling, to dissolve any remaining zinc, the solution is titrated with methylene blue solution, when oxidation proceeds from the tervalent to the quinquevalent state only and not to the usual sexavalent molybdenum (Thornton and Elderdice, *J. Amer. Chem. Soc.*, 1923, **45**, 668).

Foerster, Fricke and Hausswald (*Z. physikal. Chem.*, **146**, 95) obtained the following E_h values, Table 125, corresponding to the systems, $Mo^{VI} \rightarrow Mo^{V}$, and $Mo^{V} \rightarrow Mo^{III}$ at the respective points when $\dfrac{[Mo^{V}]}{[Mo^{VI}]}$ and $\dfrac{[Mo^{III}]}{[Mo^{V}]}$ are each equal to unity, in solutions of hydrochloric acid.

TABLE 161

REDOX POTENTIALS OF TER-, QUINQUE- AND SEXA-VALENT MOLYBDENUM

Conc. HCl.	$E_h.$	
	$Mo^{VI} \rightarrow Mo^{V}.$	$Mo^{V} \rightarrow Mo^{III}$
2N	$+ 0.532$	$+ 0.114$
4N	$+ 0.551$	$+ 0.176$
8N	$+ 0.697$	$+ 0.266$

The precise nature of the ions taking part in the two systems is largely a matter of conjecture, but the data show that in each case an increase in the concentration of acid raises the E_h values. It at once becomes apparent why methylene blue is able to oxidise to the quinquevalent stage, but fails in the more acid solutions to carry the oxidation forward to the final stage. Owing to the colours of the reduced molybdenum solutions, a series of

colours is observed before the dark green colour, produced by the first drop in excess of methylene blue and the yellow colour of quinquevalent molybdenum chloride, marking the end-point, is reached.

(b) As Indicator Only.

Lane and Eynon (*J. Soc. Chem. Ind.*, 1923, **42**, 32T) showed that Fehling's Solution can be titrated at 100° with solutions of
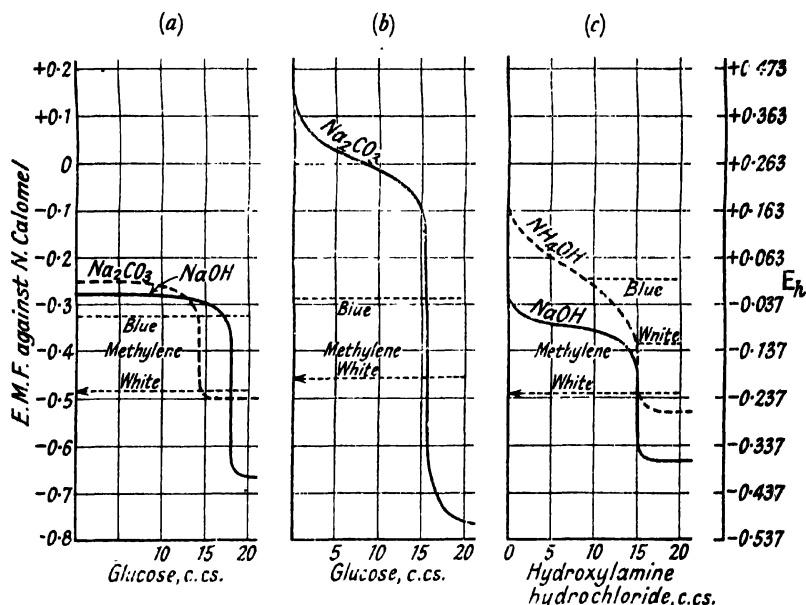
Fig. 100.—To illustrate the use of Methylene Blue in " Redox " Titrations in Alkaline Solution.

glucose and other reducing sugars, the end-point being indicated by the disappearance of the deep blue colour of the methylene blue introduced into the reaction mixture just before reaching the end-point. The redox potentiometric curve of such a titration at 90° is illustrated in Fig. 100 (*a*). The particular curve is marked NaOH, whereas the curve marked Na_2CO_3 refers to the same titration in which an equivalent amount of Na_2CO_3 was substituted for the NaOH in the Fehling's Solution. The effect of the diminished *p*H, thereby produced, is seen in the reduced titre of glucose and the less negative potentials when an excess of the glucose had been added (Britton and Phillips, *Analyst*, 1940, **65**, 18).

Owing to the considerable effect which the elevated temperature has on K_w (see p. 55, Vol. I), the pH of the Fehling's Solution is about 11 at 90° C. Fig. 100 shows that at 30° the apparent normal redox potential of methylene blue is about − 0·12. Assuming that temperature has but little effect on this value, say, to lower it by 0·03 to − 0·15, it follows that at 90° the potential, E_h, at which methylene blue is just reduced, should be given by $E_h = − 0·15 − 0·075 = − 0·225$. Taking + 0·265 volt as the potential of the N-calomel at 90°, it follows that the platinum electrode with respect to the N-calomel electrode is − 0·225 − 0·265 = − 0·490 volt. Potentiometric titration in an atmosphere of nitrogen has shown this to be the case, though it should be stressed that under the E_h conditions then prevailing the indicator is very susceptible to air-oxidation with the consequent regeneration of the blue colour. Errors may be avoided by titrating boiling solutions.

Fig. 100 (*b*) refers to the " redox " titration of potassium ferricyanide in sodium carbonate solution with glucose, and, as shown, its end-point may be detected by the decolorisation of methylene blue (Britton and Phillips, *Analyst*, 1940, **65**, 149). The curve, marked NaOH, in Fig. 100 (*c*), represents the E_h conditions during the titration of alkaline copper sulphate-sodium tartrate solutions when reduced with hydroxylamine salts (Britton and Königstein, *J. Chem. Soc.*, 1940, 673), nitrous oxide being evolved. Similar curves were obtained in the reduction by hydrazine salts of Fehling's solutions with the production of nitrogen. The E_h at the inflexions show that methylene blue is applicable to the detection of the end-points. The curve, marked NH₄OH, is typical of titrations of ammoniacal copper sulphate solutions with these reducing agents at 90°.

(ii) Diphenylamine and Allied Compounds.

The former need for an external indicator in the titration of ferrous salts with potassium dichromate has, with the introduction of a convenient internal indicator, *viz.*, diphenylamine, disappeared. The colour change, which is from almost colourless to a deep violet blue, has been investigated by Knop (*J. Amer. Chem. Soc.*, 1924, **46**, 263), Thiel (*Z. Elektrochem.*, 1929, **35**, 274), Riehm (*Z. anal. Chem.*, 1930, **81**, 353, 439) and Kolthoff and Sarver (*J. Amer. Chem. Soc.*, 1930, **52**, 4179). The transition point is at $E_h ⋯ + 0·76$. A perusal of Fig. 96 shows that this potential does not appear on the equivalence inflexion of the Fe·· − $K_2Cr_2O_7$ curve, but instead, an E_h of 0·76 volt corresponds with the oxidation of 60 per cent. of the ferrous ions. To render

the indicator serviceable, it is necessary to add to the solution an excess of either phosphoric acid or ammonium fluoride. This causes the ferric ions as they are formed to become entrapped as complex ions and thus maintains the ratio, $[Fe^{\cdot\cdot}]/[Fe^{\cdot\cdot\cdot}]$, high. Hence, during the first part of the titration, the potential, E_h, remains tolerably constant, as shown by the broken line in Fig. 96, and thus lengthens the E_h inflexion so that it includes the transition potential of the indicator. A difficulty accompanying the use of ammonium fluoride is that, although it leads to a more definite colour change, the rate at which the change occurs is slow, and it is necessary to wait a few seconds before making further additions of dichromate when in the vicinity of the end-point. The end-point is given by a medium blue, the deep blue being obtained only by back-titrating with ferrous sulphate solution.

Diphenylamine dissolves in water to the extent of 0·04 gram per litre at 15°. For use as an indicator 1 gram is dissolved in 100 c.c. of concentrated sulphuric acid, two or three drops of the solution so obtained being sufficient for a titration. Phosphoric acid, instead of sulphuric acid, has also been advocated.

According to Knop the most satisfactory titration of ferrous salts with potassium dichromate is obtained by taking a volume of ferrous salt, containing 0·1–0·15 gram of Fe ; acidifying with 20–25 c.c. of either diluted sulphuric acid (1 part H_2SO_4 : 4 parts H_2O) or 20 c.c. of diluted hydrochloric acid (1:1) ; diluting to 150–250 c.c. ; and adding 15 c.c. of phosphoric sulphuric acid mixture (150 c.c. of concentrated sulphuric acid (s.g. 1·84) + 150 c.c. of phosphoric acid (s.g. 1·7) + 700 c.c. of water).

The volumetric estimation of ferric salts by reduction with stannous chloride in strongly acid solutions, followed by the removal of the stannous chloride by precipitating with mercuric chloride, before titrating with potassium dichromate has been stated by Knop to be satisfactory, but Kolthoff and Sarver claim that mercuric ions retard the colour change.

The mechanism of the colour change of diphenylamine is complex. It is considered that before the reversible reaction responsible for the change in colour occurs, an irreversible reaction takes place in which two molecules of diphenylamine are oxidised thus :

$$2(C_6H_5)_2NH + O \rightarrow C_6H_5.NHC_6H_4C_6H_4HN.C_6H_5 + H_2O$$

to colourless diphenylbenzidine.

The reversible change to diphenylbenzidine violet thus appears to be similar to " redox " organic systems discussed earlier in

this chapter. There is a possibility that the slightly soluble green compound, occasionally obtained, is an intermediate product of this reaction.

$$\rightleftharpoons \langle \rangle N = \langle \rangle \times \langle \rangle = N \langle \rangle + 2H^{\cdot}$$

Lang (*Z. anal. Chem.*, 1931, **86**, 288 ; 1934, **97**, 395 ; 1936, **104**, 1) suggests that, instead of using diphenylamine as the indicator, it is better to convert it into the diphenylbenzidine stage in solution, by subjecting a volume of the diphenylamine indicator to the titration reaction, for which the modified indicator is subsequently to be used, until the intermediate green coloration is produced which occurs just before the characteristic deep blue coloration is obtained. Willard and Young (*Ind. Eng. Chem., Anal. Edn.*, 1932, **4**, 187) adopt a similar procedure in using diphenylamine sulphonic acid.

Owing to the appreciable oxidation involved in the use of diphenylamine it is necessary for accurate work to ascertain the magnitude of the error. To some extent, the error is minimised by using diphenylbenzidine, but probably on account of its sparing solubility its colour change in direct oxidation titrations is slow, although in reverse, or reduction, titrations the change from blue to colourless is as spontaneous as with diphenylamine.

Barium diphenylamine *p*-sulphonate (Kolthoff and Sarver, *J. Amer. Chem. Soc.*, 1931, **53**, 2902) is readily soluble in water, and moreover yields a sharp change in colour to a reddish-violet, which is so intense that it is not obscured in highly coloured solutions. As shown in Table 160 the transition potential is the same as that of diphenylamine, and therefore in order to use it in dichromate titrations it is essential that the ferric ions be removed as complexes.

As may be expected, diphenylamine may be used with advantage in oxidation or reduction titrations which give a well-defined inflexion at the equivalence-point. Thus Someya (*Z. anorg. Chem.*, 1926, **152**, 368, 382, 386 ; 1927, **160**, 355) has shown that titanous, stannous, chromous, cuprous and uranous salts may be titrated with potassium dichromate in the presence of diphenylamine. It may also be used in conjunction with other oxidising agents such as ceric sulphate and potassium permanganate. As diphenylamine changes to the blue colour at an E_h value much below that at which hydrochloric acid is oxidised by permanganate, it is especially useful in titrating ferrous salts

in hydrochloric acid solution, although, of course it is essential to use phosphoric acid.

Another excellent example of the value of diphenylamine is in the titration of vanadates with ferrous sulphate (Furman, *Ind. Eng. Chem.*, 1925, **17**, 314). Reference to Fig. 97 shows that in very acid solutions vanadates are reduced by ferrous sulphate giving at 45° an inflexion at $E_h = ca. + 0.85$. The inflexion thus occurs at a value higher than $+ 0.76$ required by diphenylamine, but by including sufficient phosphoric acid in the titration mixture to remove the ferric ions therefrom, the inflexion can be extended downwards appreciably through $+ 0.76$, and consequently renders possible the application of diphenylamine.

Of the substituted diphenylamines which have " redox " indicator properties, reference should be made to *p*-nitrodiphenylamine which on oxidation yields an intense reddish-violet compound. Walden, Hammett and Edmonds (*J. Amer. Chem. Soc.*, 1934, **56**, 1092), found that the introduction of the nitro-group raises the transition potential of the indicator by 0.3 volt. It gave excellent results in the titration of ferrous salts with ceric sulphate. Syrokomsky and Stiepin (*ibid.*, 1936, **58**, 918) state that phenylanthranilic acid (*o*-diphenylamine carboxylic acid), which changes from colourless to pink or pinkish-violet, can be used with the oxidising agents, dichromate, permanganate and ceric sulphate, and, moreover, owing to its high transition potential, 1.08 volt, can be used with ferrous salts without phosphoric acid.

(iii) Triphenylmethane Derivatives.

The majority of the indicators given in Table 160 belong to this class and owe their introduction as " redox " indicators to Knop (*Z. anal. Chem.*, 1929, **77**, 111 ; 1931, **85**, 253). In acid solution they change from a yellow or green to a pink or orange. Unfortunately, their transition potentials are of the order of 1.0 volt and they are consequently restricted in their application to the oxidising agents stronger than dichromate. 0.1 per cent. aqueous solutions are suitable for use as indicators. Indicator errors are negligibly small.

Erioglaucin A and eriogreen B can be used in ferrocyanide · permanganate titrations, so much so that DeBeer and Hjort (*Ind. Eng. Chem., Anal. Edn.*, 1935, **7**, 120) recommend this titration as a method of standardising dilute solutions of potassium permanganate. Eriogreen B is sluggish in the region of the end-point, but resists the destructive effect of permanganate more readily than does erioglaucin A. According to Furman and Wallace

(*J. Amer. Chem. Soc.*, 1930, **52**, 2347), both erioglaucin A and cyanole blue FF serve admirably in ceric sulphate titrations of ferrous salts or *vice versa*, and Kolthoff and Sandell (*Ind. Eng. Chem., Anal. Edn.*, 1930, **2**, 140) state that eriogreen B and setopalin provide more distinct end-points in the permanganate titration of arsenious acid than can be obtained alone.

(iv) Tri-*o*-phenanthroline Ferrous Sulphate.

Blau (*Monatsh.*, 1898, **19**, 647) prepared red complex salts, tri-*o*-phenanthroline ferrous sulphate and tri-α-α′-dipyridyl ferrous sulphate by the interaction in aqueous solution of ferrous sulphate and *o*-phenanthroline,
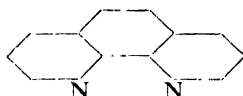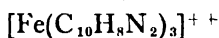
and αα′-dipyridyl, respectively. He considered that the complex cations, tri-*o*-phenanthroline ferrous ion,

$$[\mathrm{Fe}(\mathrm{C_{12}H_8N_2})_3]^{++},$$

and tri-αα′-dipyridyl ferrous ion,

$$[\mathrm{Fe}(\mathrm{C_{10}H_8N_2})_3]^{++}$$

in consequence existed in their respective solutions. Although the corresponding ferric ions cannot be formed in a comparable manner, Blau considered that the change in colour from dark red to light blue on oxidation pointed to the production of complex ferric ions, of the same composition, but which, of course, carried three positive electrical charges. The " redox " system may therefore be represented

$$\mathrm{FeX_3^{\cdots}} \rightarrow \mathrm{FeX_3^{\cdot\cdot}} + \mathrm{1FE_{FeX_3^{\cdots} \rightarrow FeX_3^{\cdot\cdot}}},$$
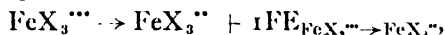
X representing a molecule of either phenanthroline or αα′-dipyridyl. The colour changes of the two systems should therefore occur at E_h values which are independent of the hydrogen-ion concentration of the solution, unless secondary difficulties arise such as the decomposition of the complex cations by acids. In 1 M.-$\mathrm{H_2SO_4}$, Walden, Hammett and Chapman (*J. Amer. Chem. Soc.*, 1931, **53**, 3908 ; 1933, **55**, 2649) found that the transition potential of the ferrous phenanthroline system was $E_h = 1\cdot14$ volts in the case of a ceric sulphate titration of ferrous sulphate. Increasing concentration of acid causes a fall in the transition potential (Walden, Hammett and Edmonds, *ibid.*, 1934, **56**, 57). The αα′-dipyridyl ferrous salt is decomposed more readily by

acids ; its transition potential is indefinite, and its use as a " redox " indicator is greatly inferior to ferrous *o*-phenanthroline sulphate.

For use as an indicator, Walden *et al.* recommend an aqueous solution of ferrous sulphate and *o*-phenanthroline monohydrate in the molecular ratio of 1 : 3, the solution being 0·025 M. with respect to ferrous sulphate. Such a solution, if used to the extent of 1 drop per 200 c.c. of solution undergoing titration, which incidentally gives the best colour change, eliminates the need for indicator correction when the oxidising agent is decinormal.

The indicator behaves satisfactorily in conjunction with ceric sulphate, potassium permanganate and even potassium dichromate. To make full use of its colour change with potassium dichromate it is necessary, as Fig. 96 shows, to extend the end-point inflexion upwards as much as possible, and this can only be effected by an increased acid concentration. In titrating ferrous salts, phosphoric acid is, of course, unnecessary. In this titration the colour changes from yellow through brownish green to bluish green. The change is somewhat sluggish at the end-point, which can be overcome by allowing sufficient time, a few seconds, between each addition of oxidant or by overstepping the end-point and then titrating back with ferrous sulphate.

(v) Other " Redox " Indicators.

A number of more or less irreversible compounds have been employed as " redox " indicators. Among them are methyl orange and methyl red, which have been used for potassium bromate titrations (see Smith and Bliss, *J. Amer. Chem. Soc.*, 1931, **53**, 2091, 4291) ; methylene blue and Congo Red for ceric titrations (Rathsburg, *Ber.*, 1928, **65**, 1663 ; Willard and Young, *J. Amer. Chem. Soc.*, 1928, **50**, 1322 ; Furman and Wallace, *ibid.*, 1930, **52**, 1443, 2347 ; Furman, *ibid.*, 1932, **54**, 4235) ; brucine (1 per cent. in 3 N-H_2SO_4) in dichromate titrations, and in titrations of ferrous iron in hydrochloric acid solutions with potassium permanganate (Narayanamurthi and Seshadri, *Proc. Indian Acad. Sci.*, 1936, 3A, 38) ; benzopurpurin B and 4B for titrations of tin and antimony with potassium bromate (Raichinschtein, *J. Appl. Chem., Russia,* 1935, **8**, 1470).

CHAPTER XXIII

POTENTIOMETRIC TITRATIONS OF ACIDS AND BASES IN NON-AQUEOUS SOLVENTS

MANY organic acids and bases form salts in non-aqueous media. Owing to the exceptional weakness of either the acid or the base, or of both, in aqueous solution, the formation of a salt does not always take place therein. Moreover, the acid or base may be so extremely weak that its strength in aqueous solution cannot be determined by the available physico-chemical methods. The solvent must therefore play an important part in such acid-base neutralisations, and it must be inferred that in certain non-aqueous solvents the strength of these very weak acids and bases must be appreciably increased in order for them to react with one another. This, indeed, must be the case, for, as we shall see, some very weak acids and bases, *e.g.*, phenol and urea, acquire increased strength in non-aqueous media. Even strong acids may become stronger. Thus in aqueous solution very little difference in strength can be detected between hydrochloric acid and perchloric acid, yet in many non-aqueous solvents perchloric acid behaves as a much stronger acid than hydrochloric acid.

The influence which the dielectric constant of a solvent has on the ionisation of an acid, base or salt, depends on the magnitude of the dielectric constant of the solvent. This follows from the Inverse Square Law of Coulomb and it has been rendered in a generalised form in the so-called J. J. Thomson-Nernst Rule (1893), *viz.*, that " the ionising power of a solvent is greater the larger the dielectric constant." It would be expected, therefore, that water with its dielectric constant of 81 would be a far better ionising medium than either methanol, $D = 33$, or ethanol, $D = 26 \cdot 1$, or benzene, $D = 2 \cdot 3$..

As the dielectric constant of water is much larger than that of non-aqueous solvents, it is obvious that there must be at least another factor which operates in promoting the ionisation of acids and bases. This appears to be the readiness with which ions are solvated and especially the hydrogen-ion, which in its simplest state is the proton, and the hydroxyl-ion. Such solvation of ions is more likely to occur with a solvent, the molecules of which are polar, than with non-polar solvents. The Lowry-Brønsted

32

theory of acids and bases (Vol. I, p. 347) is, in essence, merely a statement that a proton is solvated by a single molecule of a solvent, thus

$$H^+ + H_2O \rightarrow H_3O^+$$

or

$$H^+ + Sv \rightarrow HSv^+$$
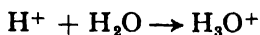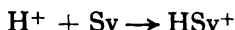
Sv being a molecule of solvent. No experimental proof has, as yet, been advanced for the contention that a proton is solvated by one molecule only of solvent as it exists in solution.

Much attention has recently been given to the possibility of following acid-base reactions in non-aqueous media potentiometrically. This may be attributed not only to the growing interest in potentiometric methods but to the ease with which valve-voltmeters, in particular many pH meters, can be adapted for the measurement of the E.M.F.s of cells containing solutions in non-aqueous solvents. It happens that the electrical conductance of these solutions is usually low, which, in introducing a high resistance in the circuit, renders difficult the measurement of the E.M.F. by means of the ordinary Poggendorf potentiometer and it is for this reason that valve amplification has been advantageous.

Many authors have attempted to interpret the potentials set up at indicator electrodes during the neutralisation of an acid with a base, or vice-versa, in terms of " apparent pH scales," but in the present state of our knowledge such scales can be little better than qualitative. The E.M.F.s themselves should suffice to show the changes in acidity or alkalinity that ensue during a titration.

In general, electrometric titration curves have well-defined inflexions at the equivalence points. As is shown later, the work so far done reveals the possibility of potentiometric methods in organic chemical analysis and in industrial chemistry. Thus electrometric titration provides a useful means of determining the contents of acids (or bases) in oils and other substances such as shellac which are insoluble in water. The method is particularly invaluable in dealing with dark coloured oils and asphalts, for which volumetric methods involving indicators are difficult and often unreliable.

The indicator electrodes which have been used are : (a) the hydrogen electrode, (b) the quinhydrone electrode, (c) platinum electrodes alone, possibly functioning as a kind of oxygen electrode, (d) the glass electrode, (e) the chloranil electrode, and (f) the antimony electrode.

A disadvantage of cells containing non-aqueous media is their

high electrical resistance, which makes the measurement of their E.M.F. by the usual potentiometric method difficult. This, however, can be overcome by employing valve amplification. Another way of overcoming this difficulty is to select a solvent which has a high dielectric constant, in order to promote the ionisation of the solute, and further to increase the electrical conductivity by dissolving a neutral salt in the medium. N-butyl alcohol, dielectric constant, $D = 18$, and *iso*-amyl alcohol, $D = 15$, are often employed, especially when saturated with lithium or potassium chloride.

Either of the calomel electrodes or the Ag|AgCl electrode will serve as reference electrode. In performing acid-base electrometric titrations in aqueous solutions Holt and Kahlenberg (*Trans. Amer. Electrochem. Soc.*, 57, 361) observed that the potentials of carbon and graphite electrodes and of the silver electrode did not change to any great extent as the pH of the solution, undergoing titration, was varied. Such electrodes could therefore be used as reference electrodes in conjunction with an electrode which is sensitive to changes in hydrogen-ion concentration, *viz.*, platinum or air electrode, antimony and tungsten electrodes. For the purpose of an electrometric titration, it is only necessary therefore to immerse, say, a platinum and a graphite electrode in the solution to be titrated and to measure the E.M.F. between the two as the titration proceeds. Ralston, Fellows and Wyatt (*Ind. Eng. Chem., Anal. Edn.*, 1932, 4, 109) have applied the platinum-carbon electrode system to the electrometric determination of the acidity of oils and titration of acids in non-aqueous media. Carbon and natural graphite electrodes gave equally good results, whilst, owing to their compactness, high electrical conductivity and low resistance-contact with the solution, arc-lamp carbons proved very serviceable. Moss, Elliot and Hall (*Anal. Chem.*, 20, 784) used an antimony electrode as that of reference. It was maintained at constant potential by allowing the titrant to flow over it as the titrant left the burette, the tip of the burette making contact with the solution undergoing titration. The electrode was inserted in a tube at right angles to the outflow tube of the burette.

Ordinary calomel reference electrodes, especially the Saturated Calomel, are now used (Hall and Conant, *J. Amer. Chem. Soc.*, 49, 3047). Although they used the platinum-chloranil electrode as indicator electrode they found it necessary to employ a Compton electrometer for the measurements of the E.M.F. of their cells in which the solvent was glacial acetic acid.

Some workers have used the same solvent throughout the cell combination and have therefore improvised reference electrodes incorporating the particular solvent. Examples of such electrodes are Ag|AgCl.CH$_3$OH solution of NaCl (Ogston and Brown, *Trans. Faraday Soc.*, 1935, **31**, 574); Hg|Hg$_2$Cl$_2$ + saturated solution of LiCl in 95 per cent. ethyl alcohol (Gardner and Whitmore, *Ind. Eng. Chem., Anal. Edn.*, 1929, **1**, 205 ; Caldwell, *ibid.*, 1932, **4**, 52); Pt|Quinhydrone dissolved in amyl alcohol (Seltz and McKinney, *ibid.*, 1928, **20**, 542); Ag|AgCl.*n*-butyl alcohol solution of LiCl (Seltz and Silverman, *ibid.*, 1930, **2**, 1) and Pt|Quinhydrone dissolved in 0·003 M.-picric acid in *n*-butyl alcohol + a trace of water (Evans and Davenport, *ibid.*, 1936, **8**, 287). The last electrode was used with the glass electrode, and the small amount of water added was sufficient to ensure the proper functioning of the glass electrode (*cf.* Dole, *J. Amer. Chem. Soc.*, 1932, **54**, 3095). In some cases the " salt bridge " has consisted of a solution of a neutral salt in a non-aqueous solvent. These refinements are quite unnecessary and, in fact, increase the resistance of the cell as a whole, with the result that the measurement of the E.M.F. is made increasingly difficult, such that resort may have to be made to valve amplification, which some workers have found necessary. Amplification is necessary with the glass electrode, unless a ballistic galvanometer is used in conjunction with a condenser. The " salt bridge ", consisting of a saturated solution of potassium chloride, with each end of the U-tube plugged with filter paper is usually quite satisfactory.

The hydrogen electrode has been used by Gardner and Whitmore (*loc. cit.*) to titrate alcoholic solutions of shellac with alcoholic potash, and by Whitmore, Weinberger and Gardner (*Ind. Eng. Chem., Anal. Edn.*, 1932, **4**, 48) to titrate saponified shellac with hydrochloric acid. The curve showed the decomposition of the potassium salt as the acid was added. Demarest and Rieman (*ibid.*, 1931, **3**, 15) used the electrode for the titration of saponified drying oils (*e.g.*, linseed) and asphalt with hydrochloric acid. Anisole was the most suitable solvent. Methyl alcohol solutions of ammonia, monochloroacetic acid, anthranilic acid and tyrosine, and ethyl alcohol solutions of tyrosine and glycine have been titrated (Ogston and Brown, *loc. cit.*). Newbery's type of hydrogen electrode (*Trans. Electrochem. Soc.*, 1933, **64**, 209) was used in anhydrous ethylenediamine solutions by Moss, Elliot and Hall (*loc. cit.*). It consisted of platinised gold which was supplied with hydrogen through a sintered glass bubbling tube placed under the electrode. They also state that their most practical and serviceable electrodes consisted of stainless

steel tubes, 10 mm. diameter and 10 cm. in length, through which
hydrogen was bubbled and made contact with the solution at the
surface of the metal discs at the lower ends. They were used
with a bright surface, no platinising being necessary.

The quinhydrone electrode has been extensively used. Seltz
et al. (*loc. cit.*) titrated oils and fats, *e.g.*, rosin oil, lard oil, trans-
former oil, butter-fat, dissolved in either butyl alcohol or amyl
alcohol, saturated with lithium chloride, with potash or lithia dis-
solved in the respective alcohol. Jarrett (*J. Oil and Col. Chem.
Assoc.*,   **23, 34**) showed that benzoic acid, dissolved in a
mixture of ethyl alcohol and benzene, can be titrated with alcoholic
potash. He also showed that the acid values of drying oils and
varnishes, dissolved in equi-volume mixtures of butyl alcohol and
benzene, could be determined by quinhydrone electrode titration
with alcoholic potash. Caldwell (*loc. cit.*) made similar observa-
tions by using a gold electrode in conjunction with quinhydrone.
The acids in lubricating oils, dissolved in *n*-butyl alcohol (+ LiCl),
and in insulating oils in solution in *n*-butyl alcohol saturated with
potassium chloride, have been electrometrically titrated by Clarke,
Wooten and Compton (*Ind. Eng. Chem., Anal. Edn.*, 1931, **3**, 321)
and Evans and Davenport (*ibid.*, 82). Thorough mixing of the
solution with the titrant is usually ensured by bubbling pure
nitrogen through the titration vessel. Reference should be made
to the thermionic valve titrometer devised by Clarke *et al.* for
non-aqueous titrations. The galvanometer deflections are noted
after the addition of each 0·5 c.c. of titrant, and the galvano-
meter is set back to zero. A differential titration curve is thus
obtained.

Attention has been directed by Ruehle (
to the choice of suitable solvents for quinhydrone electrode titra-
tion work. As shown by Demarest and Rieman, anisole is an
excellent solvent for asphalts and pitches, but when alone it
interferes with quinhydrone. The admixture of sufficient butyl
alcohol eliminates this difficulty. This is also the case with
dioxane which readily dissolves the heavier oils. Acetone-butyl
alcohol mixtures also dissolve many organic acids. Ruehle also
showed that Cellosolves (*viz.*, ethylene glycol monoalkyl ethers)
are excellent solvents for cellulose nitrate and cellulose acetate.
He demonstrated that both cellulose derivatives, dissolved in
methyl cellosolve, may be titrated with potash, similarly dissolved.
Organic acids could also be titrated.

Ruehle purifies the commercial ethylene glycol monomethyl
ether thus : add 30 grams of animal charcoal to 4 litres of solvent,
stir, filter. Add an additional 30 grams of charcoal and 500 grams

of anhydrous sodium sulphate.   Stand overnight, add 20 grams of sodium wire and distil *in vacuo* at 75° C.

The titrant is 0·05 N-KOH in purified ethylene glycol mono-methyl ether.   The lithium chloride solution is prepared by refluxing 200 grams with 1 litre of ether.   The solution to be titrated consists of 10 c.c. solution of an acid solution in ether, 10 c.c. of LiCl solution, made up to 100 c.c. with methyl cello-solve.   50 mg. of quinhydrone are added to 100 c.c. of solution.

Using amyl or butyl alcohol solutions of alkali as titrants, an inflexion is sometimes produced before the final inflexion which actually indicates the true end-point.   Wooten and Ruehle (*ibid.*, 1934, **6,** 449) have traced this inflexion to the formation of a little salt, usually of a weak acid, in the titrant and it probably originates from the oxidation, or condensation, of aldehydes present as impurities in the alcohol.   The authors suggest that a known solution of picric acid should first be titrated, using quinhydrone, with the titrant and the position of any auxiliary inflexions observed.

The glass electrode has been used by Evans and Davenport (*ibid.*, 1936, **8,** 287) for the titration of insulating cable oil, with potassium hydroxide dissolved, preferably, in methyl alcohol. They considered it to be essential that the same non-aqueous solvent should be used on each side of the glass membrane and that the solvent should contain a trace of water.   This view is no longer held and the ordinary commercial glass electrodes of the bulb type, inside of which is dilute hydrochloric acid in contact with the silver-silver chloride electrode, are now generally used. Moreover, the presence of a trace of water in the solution is not regarded as necessary, in fact many authors take particular care to exclude water from both the test solution and the titrant (*vide infra*, Lykken *et al.*).

It would seem that the glass electrode can be successfully used in almost any solvent.   Thus it has been used in methanol (Wagner, Brown and Peters, *J. Amer. Chem. Soc.*, 1947, **69,** 2611), in ethanol (Rolfe and Alcock, *J. Soc. Chem. Ind.*, 1937, **56,** 294T), in acetonitrile (Fritz, *Anal. Chem.*, 1953, **25,** 407), in glacial acetic acid (Blumrich and Bandel, *Angew. Chem.*, 1941, **54,** 37 ; Wagner, Brown and Peters, *J. Amer. Chem. Soc.*, 1947, **69,** 2609 ; Seaman and Allen, *Anal. Chem.*, 1951, **23,** 592 ;   Markunas and Riddick, *ibid.*, 337) ;   in mixtures of :   benzene and isopropyl alcohol and 1 per cent. of water (Lykken, Porter, Ruliffson and Tuemmler, *Ind. Eng. Chem., Anal. Edn.*, 1944, **16,** 219), any glycol and a solvent, *e.g.*, a hydrocarbon, alcohol or chlorinated hydrocarbon (Palit, *ibid.*, 1946, **18,** 246), ethanol and either

$C_6Cl_4O_2$, and hydrochloranil, its reduced form, is completely chlorinated hydroquinone, $C_6Cl_4(OH)_2$, so the equilibrium set up in the solution is

$$2H^{\cdot} + C_6Cl_4O_2(\text{solid}) \rightleftharpoons C_6Cl_4(OH)_2(\text{solid}) + 2F.$$
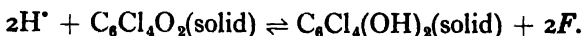
To hasten equilibrium between the redox system in the solution, the glacial acetic acid solution was previously saturated at an elevated temperature but never above $50°$ C., 0.6 gram of chloranil and 0.8 gram of hydrochloranil being always added per 100 c.c. of solution.

In a similar way to that of the quinhydrone electrode (see Vol. I, p. 22) the potential set up at an inert electrode, such as one of platinum, is a function of the hydrogen-ion activity of the solution.

When a base, B, is dissolved in glacial acetic acid an equilibrium between the base and the acid is set up, thus

$$B + HAc \rightleftharpoons BHAc \rightleftharpoons BH^{\cdot} + Ac'$$

or in terms of the Brønsted Theory, the solvent acting as an acid donates a proton to the base, thus

$$HAc + B \rightleftharpoons BH^{\cdot} + Ac'$$
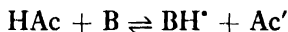
It is only in the case of bases, which are much stronger than acetic acid is as an acid, that the equilibrium will lie almost entirely on the right and that the base will exist in solution as its ionised acetate, $BH^{\cdot} + Ac'$. On titrating with a strong acid, HX, the replacement reaction,

$$BHAc + HX \rightarrow BHX + HAc$$

i.e.

$$Ac' + HX \rightarrow X' + HAc$$
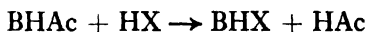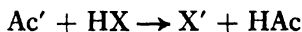
will proceed and it would be expected that the $pH_{(HAc)}$ would depend on $pK_{a_{HAc}}$ and the ratio of $a_{Ac'}/a_{HAc}$ as indicated by the equation,

$$pH_{(HAc)} = pK_{a_{HAc}} + \log \frac{a_{Ac'}}{a_{HAc}}$$

[HAc] being relatively large and constant.

With weak bases the interaction with the acetic acid will not be complete and the equilibrium will lie on the left and the displacement will increase in this direction with still weaker acids. The progressive addition of a strong acid, HX, to the solution will cause the free base, B, to undergo neutralisation, thus

$$B + HX \rightarrow BHX \rightarrow BH^{\cdot} + X'$$
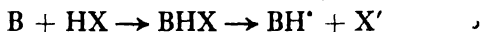
As the titration proceeds, any BHAc that was originally formed

will decompose, thereby enabling all the base which was dissolved in the glacial acetic acid to be completely neutralised. But the pH and therefore the E.M.F. of the indicator electrode will depend on the dissociation constant of the base in glacial acetic acid and $a_{BH}\cdot/a_B$,

thus
$$pH_{(HAo)} = (pK_w - pK_b) - \log a_{BH}\cdot/a_B$$
$$= pK' - \log a_{BH}\cdot/a_B$$

The weakest bases will exist in the glacial acetic acid solution as such for they are too weak to react with the acetic acid and they may be too weak to be neutralised even by so strong an acid as perchloric. In consequence, the E.M.F.s set up during their titration will be the same as those which would have been set up if the titrant had been added to the same volume of glacial acetic acid.
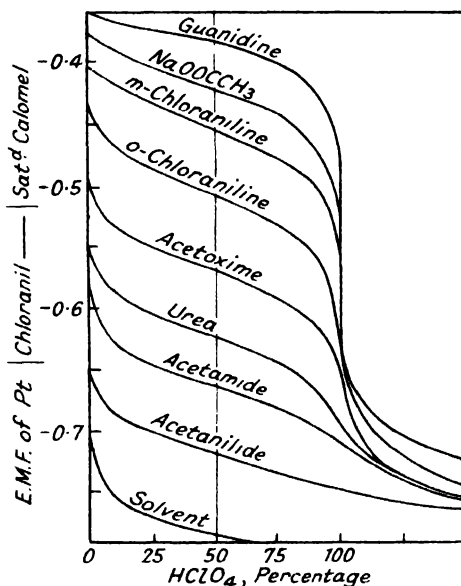

FIG. 101.—Titration of o·o5N Bases in Glacial Acetic Acid with HClO₄. (Hall and Werner, *J. Amer. Chem. Soc.*, 1928, **50**, 2367.)

In Fig. 101 are the curves which were obtained by Hall and Werner by titrating solutions of the bases, indicated thereon, in glacial acetic acid with o·2M perchloric acid. With the exception of the curves of the strong bases, guanidine and sodium hydroxide, the two uppermost and the one at the bottom, *viz.*, that of acetanilide, the shape of the curves is similar to that of weak monoacidic bases in aqueous solution. When neutralisation has proceeded

to 50 per cent., the E.M.F.s then set up might therefore be expected to be a function of $[pK_g - pK_{b_{(HAc)}}]$ and consequently they might serve as a means of comparing the strengths of the bases in glacial acetic acid, where $pK_g = [H']_g[OH']_g$, viz., the ionic product of water in glacial acetic acid.

In water, acetamide has a $pK_w - pK_b = ca.$ 15, and urea one of ca. 14. Hence on titration in aqueous solution with 0·2M perchloric acid in neither instance would the termination of the neutralisation be indicated by the slightest vestige of an inflexion. Evidently in glacial acetic acid, urea becomes a much stronger base and so must acetamide, for in both cases inflexions are discernible.

Fig. 102 shows that it is sometimes possible to titrate diacidic bases in glacial acetic acid when it is not practicable in aqueous solution. The curve is that of p-phenylenediamine. In water $pK_{b_1} = ca.$ 8 and $pK_{b_2} = ca.$ 11, which shows that therein neutralisation of the first stage would occur mainly between pH 8 and 4 and of the second stage between pH 5 and pH 1, so that

FIG. 102.—Titration of p-Phenylenediamine in Glacial Acetic Acid with Sulphuric Acid.

(Hall and Conant, *J. Amer. Chem. Soc.*, 1927, **49**, 3047.)

the inflexion indicating the end of the neutralisation of the first —NH_2 group would be somewhat indefinite and no inflexion would occur on the addition of the second equivalent of sulphuric acid. In glacial acetic acid, however, the opposite is the case. (Incidentally, during this titration the solution became brown through oxidation by the chloranil.)

Fig. 103 consists of a collection of titration curves of monoacidic bases in glacial acid. They are numbered from the bottom upwards and the bases titrated, and the numbers assigned to their respective curves are recorded in Table 162 (*vide* Hall, *J. Amer. Chem. Soc.*, 1930, **52**, 5112). It will be noticed that Fig. 103 is similar to the chart on p. 196 (Vol. I) and that the

curves in the middle of Fig. 103 are of the form that is character-
istic of moderately weak bases. It is probable that potentials at
their mid-points afford a measure of their strengths as bases,
viz., $pK_g - pK_{b(HAc)}$.
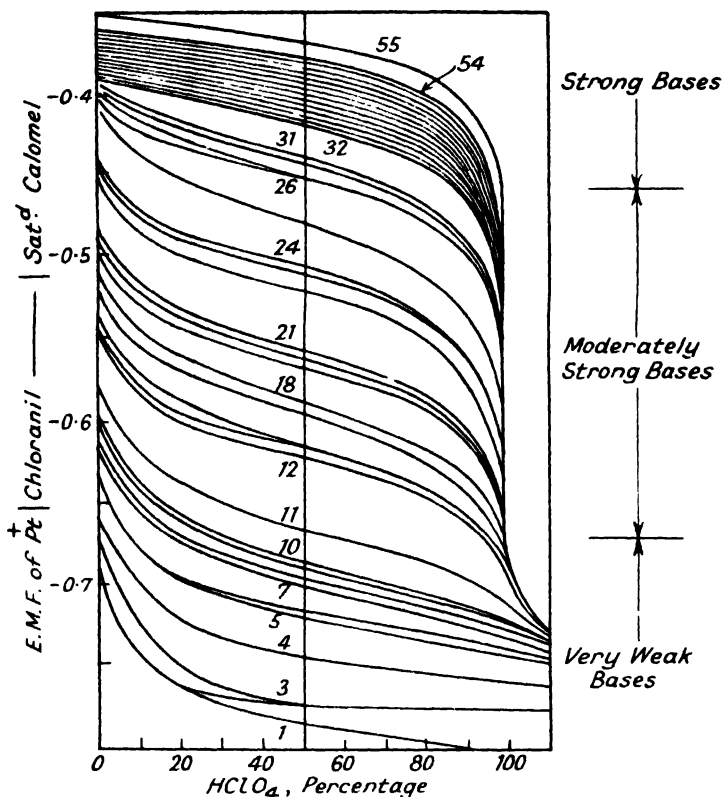

FIG. 103.—Titration of 0·05N Bases in Glacial Acetic Acid with $HClO_4$.
(Hall, *J. Amer. Chem. Soc.*, 1930, **52**, 5115.)

The curves in Fig. 103 of the bases are thus in the order of
their increasing strength. They follow the numerical sequence
given in Table 162 ; the curves of the weakest bases are at the
bottom of Fig. 103 and the strongest at the top. In Table 162
are also given the $(pK_w - pK_b)$ values for many of the bases in
aqueous solution. In general, the difference between pK_w and
pK_b increases in the same order as the E.M.F.s corresponding
to the mid-points of the curves. There are, however, notable
exceptions among the bases, Nos. 46 to 55. If there had existed

a real relationship between the strengths of bases in aqueous solution and their respective strengths in glacial acetic acid, bases 46, 48, 49, 50a, 50b should have been at the end of the list. These anomalies may be due in some way to the so-called "levelling" effect of glacial acetic acid (see page 46).

TABLE 162

ORDER OF STRENGTHS OF BASES IN GLACIAL ACETIC ACID

No.	Base	pK_w	pK_b	No.	Base.	$pK_w - pK_b$
1a	Propionitrile		0·8	32	α-Naphthylamine	4·0
1b	4-Nitro-2,6-dichloro-			33	m-Toluidine	4·7
	aniline			34	m-Anisidine	4·2
2	Anisalacetophenone			35	p-Anisidine	5·3
3a	Diacetylmonoxime			36a	Benzylaniline	
3b	Formanilide			36b	o-Toluidine	4·4
4	5-Dimethylphenylurea			37a	p-Toluidine	5·1
5	Acetanilide		·| 0·4	37b	Methylaniline	4·8
6	Tribromoaniline			38	o-Anisidine	4·5
7	n-Propylacetanilide			41	Methyl-o-toluidine	4·6
8	n-Methylacetanilide			42a	Quinoline	4·9
9	o-nitroaniline		+ 0·06	42b	Methyl-p-toluidine	5·3
10	Phenylurea			43	Ethylaniline	5·1
11	Acetamide		− 0·5	44	Dimethylaniline	5·1
12	p-Nitrodimethylaniline			45	Pyridine	5·2
13	Urea		+ 0·10	46	Dimethylamine	10·7
14	Methylurea			47	α-Picoline	6·5
15	Dimethylpyrone		+ 0·4	48	Diphenylguanidine	10·0
16	Diphenylamine		+ 0·9	49	Piperidine	11·1
17	2,5-Dichloroaniline			50a	Diethylamine	11·0
18	p-Nitroaniline		1·9	50b	Triphenylguanidine	9·1
19	Acetoxime		1·8	51	Methyl-n-propylaniline	5·6
20	2,4-Dichloroaniline			52a	Methylethylaniline	6·0
21a	3-Nitro-4-chloroaniline			52b	p-Aminodimethylaniline	6·5
21b	Colchicine		1·7	52c	Ammonia	9·3
22	m-Dinitrodimethylaniline			52d	Tri-n-butylamine	9·9
23	o-Bromoaniline		2·6	52e	Di-n-butylamine	11·2
24	o-Chloroaniline		2·8	52f	Guanidine	13·5
25	Antipyrine		1·5	53a	Di-n-propylaniline	5·6
26	m-Chloroaniline		3·5	53b	Dimethylaniline	6·5
27	m-Bromoaniline		3·5	53c	Triethanolamine	7·8
28	p-Nitrosodiphenylamine			54a	Dimethyl-o-toluidine	5·9
29	Semicarbazide		3·7	54b	Dimethyl-p-toluidine	7·1
30	p-Chloroaniline			54c	Triethylamine	10·7
31	p-Bromoaniline			55	Dimethyl-o-toluidine	7·2

In aqueous solution, little difference between the strengths of perchloric acid and hydrochloric acid can be detected by physico-chemical methods, but sulphuric acid is decidedly weaker than either acid and this is especially true of its second stage of dissociation. In glacial acetic acid, however, as Fig. 104 shows, perchloric acid is stronger than sulphuric acid which in turn is stronger than hydrochloric acid. This is seen by the potentials set up at the chloranil electrode when N. solutions in glacial acetic acid of the three acids were added to glacial acetic acid

alone, *i.e.* the blanks, *A*, *B* and *C*, and subsequently by the final potentials established when 0·05M solutions of the acids were used in titrating the bases shown on the curves. It will be observed that in the case of the two weakest bases, acetoxime and urea, a small inflexion only can be detected in curve *C* for acetoxime and none at all in the curve *C* for urea. The inflexion is markedly improved in curve *A* for acetoxime and becomes apparent in curve *A* for urea.
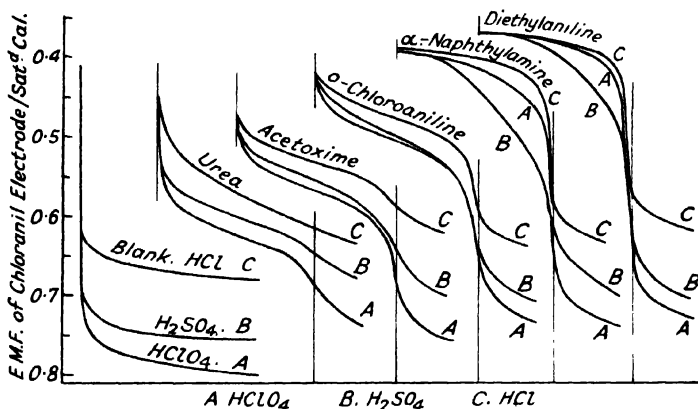

FIG. 104.—Chloranil Electro-titrations of Bases of Different Strengths in Glacial Acetic Acid with *A*, Perchloric Acid, *B*, Sulphuric Acid, *C*, Hydrochloric Acid.

(Hall and Werner, *J. Amer. Chem. Soc.*, 1928, **50**, 2367.)

Corroborative evidence of the fact that in glacial acetic acid perchloric acid is a very strong acid was obtained by Kolthoff and Willman (*J. Amer. Chem. Soc.*, , **56**, 1007, 1014), who concluded from their electrical conductivity measurements of solutions of various acids in glacial acetic acid that the order of acid-strength is :

$$HClO_4 > HBr > H_2SO_4 > HCl > HNO_3.$$

The glass electrode is also quite effective for titrations with a strong acid of bases, dissolved in glacial acetic acid (Blumrich and Bandel, *Angew. Chem.*, 1941, **54**, 374 ; Wagner, Brown and Peters, *J. Amer. Chem. Soc.*, 1947, **69**, 2609 ; Markunas and Riddick, *Anal. Chem.*, 1951, **23**, 337 ; Seaman and Allen, *ibid.*, 952).

Blumrich and Bandel after determining the titre of primary, secondary and tertiary amines in a glacial acetic acid solution, by potentiometric titration, took another portion of the amine solu-

tion, acetylated it with acetic anhydride, and then titrated the remaining tertiary amine by potentiometric titration with perchloric acid. Wagner, Brown and Peters confirmed and extended the method of Blumrich but used hydrochloric acid as titrant. Seaman and Allen showed that perchloric acid solutions could be standardised by glass electro-titration of potassium hydrogen phthalate in a glacial acetic acid solution.

Markunas and Riddick claim to have titrated some 400 compounds in glacial acetic acid with perchloric acid. Besides all types of organic bases their investigations included the salts, ammonium acetate, benzoate, citrate, and salicylate, sodium acetate, formate, and benzoate, guanidinium acetate and 8-hydroxyquinoline benzoate. They state that the presence of water in either the test solution or titrant affected the accuracy of the titrations, but it was not influenced if the water-content was kept below 1·5 per cent.

To prepare o·1N.HClO$_4$ solution in glacial acetic acid Markunas and Riddick recommend the following method : add 14·5 grams of 70–72 per cent. perchloric acid solution to about 900 c.c. of glacial acetic acid in a litre flask, then add acetic anhydride slowly, while swirling the flask, in an amount that is sufficient to combine with the water introduced with the aqueous perchloric acid and finally dilute to the mark with glacial acetic acid. Allow to stand for 24 hours and standardise either by glass electro-titration of potassium hydrogen phthalate or by titration using crystal violet as indicator (1 gm. per 100 c.c. of glacial acetic acid).

Because coal tar, asphalts, petroleum and shale oils are themselves usually insoluble in glacial acetic acid, Zeal, Weiss and White (*Anal. Chem.*, 25, 426) found that they could be dissolved in benzene or monochlorobenzene and then mixed with an equal volume of glacial acetic acid and titrated by means of the glass electrode with either perchloric or hydrochloric acid. If, however, benzene is used, special shielding devices are necessary. Chlorobenzene is preferable, but difficulties, through inadequate shielding, arise if the amount used exceeds 50 per cent. by volume. They state that although the inflexion with a weak nitrogen base is larger in chlorobenzene alone than in the solvent mixture, the latter advantage does not outweigh the serious disadvantage of the resulting instability of the glass electrode in pure chlorobenzene. The hydrochloric acid solution used as titrant was dissolved in isopropylalcohol. Fig. 105 illustrates the kind of curve which they obtained, the upper one referring to a titration of a mixture of sodium hydroxide, piperidine and quinaldine, whilst the lower curve is that of piperidine alone when titrated with hydrochloric acid.
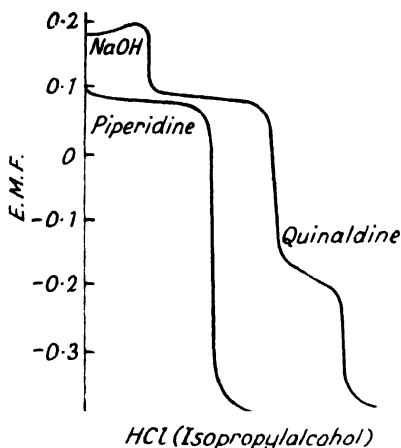
FIG. 105.—Glass Electro-titration of Bases in Glacial Acetic Acid + Mono-chlorobenzene 50 : 50.

(Zeal, Weiss and White, *Anal. Chem.*, 1953, **25**, 426.)

Figs. 106 and 107, which are reproduced from a paper by Pifer, Wollish and Schmall (*Anal. Chem.*, 1953, **25**, 310), illustrate the effect of an admixture with glacial acid of other solvents, either in the solution undergoing titration or in the titrant. In Fig. 106, the curves labelled " H_2O " are those of titrations of solutions of o·200 gram of sodium acetate dissolved in 50 c.c. of water with o·1 N . $HClO_4$ in ethanol (top curve) and with o·1 N . $HClO_4$ in dioxan (bottom curve). The use of solvents containing 90 per cent. of either ethanol or dioxan greatly increases the size of the inflexions but they are increased still more by replacing the 10 per cent. of water with
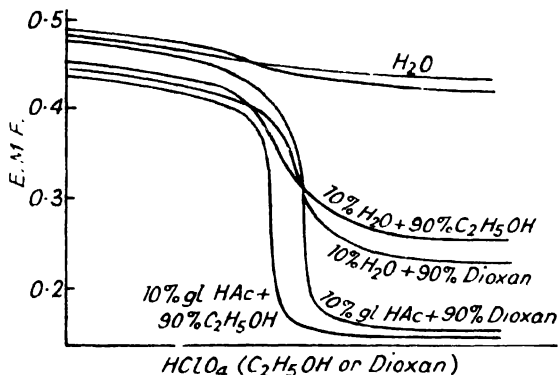

FIG. 106.—Effect of Solvent. Glass Electro-titrations of NaOOCCH₃ in various solvent mixtures.

(Pifer, Wollish and Schmall, *Anal. Chem.*, 1953, **25**, 310).

10 per cent. of glacial acetic acid. Fig. 106 shows that when a glacial acetic acid solution is used, care must be taken either to use glacial acetic acid for the titrant or else some other solvent, such as dioxan, which has been proved not to impair the inflexions.

One of the disadvantages in using glacial acetic acid as a solvent is the so-called "levelling effect" which is exercised

when two or more bases are sufficiently strong to react almost completely with the acetic acid.   On titrating with a strong acid, such as perchloric, no inflexion marking the end of the reaction with the acetate formed with either base occurs but only the final inflexion corresponding to the complete replacement of the acetate-ion by that of the anion of the strong acid.   This is seen in Fig. 111, in which no inflexion occurs with the first equivalent but only with the second equivalent of acid per molecule of quinine when the solvent is glacial acetic acid ; but when it is ethanol or,
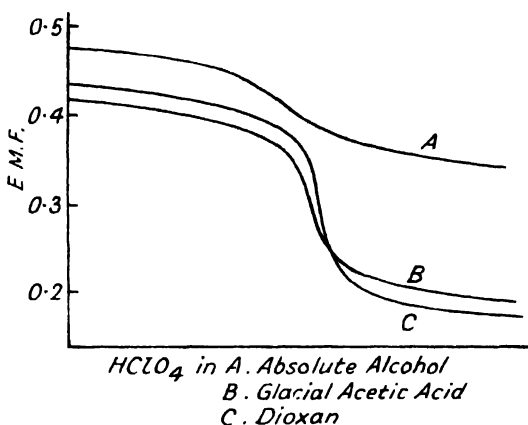

$HClO_4$ in A. Absolute Alcohol
B . Glacial Acetic Acid
C . Dioxan

FIG. 107.—Glass Electro-titrations of NaOOCCH₃
(o·2 gm. in 50 c.c.) in Glacial Acetic Acid with Perchloric Acid in different Non-aqueous Solvents.
(Pifer, Wollish and Schmall, *Anal. Chem.*, 1953, **25**, 310.)

better still, chloroform, inflexions corresponding to the addition of the first and second equivalents of perchloric acid are produced.

We shall now discuss a basic solvent, ethylenediamine.   Although chosen by Moss, Elliot and Hall (*Anal. Chem.*, 1948, **20**, 784) for the reason that it is an excellent solvent for synthetic resins (*e.g.*, those containing phenol and a dicarboxylic acid), it has proved useful in the titration of acids and amino-acids with sodium hydroxide.   Moss *et al.* tried other basic solvents, *viz.*, diamylamine, pyridine and ethanolamine, but found that better end-point inflexions were obtainable with ethylenediamine and especially when it was free from moisture.   The dielectric constant of ethylenediamine is about 16.

A difficulty encountered with this medium, however, is that it is not a good solvent for sodium hydroxide.   A suitable alkali titrant can, however, be prepared by dissolving about 2·5 grams of sodium by successive treatment with ethanol and ethanolamine

and then making up to 100 c.c. with ethanolamine.   After cooling,
the solution is diluted with ethylenediamine to 500 c.c.   To
ensure that the solution remains clear on standing, 10–20 per cent.
of its total volume should be ethanolamine.

In ethylenediamine solutions, the glass electrode was not satis-
factory but both the hydrogen and antimony electrodes proved
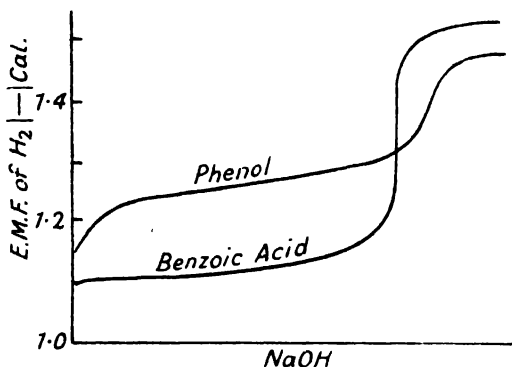serviceable.   Figs. 108 and 109, obtained with the hydrogen

FIG. 108.—Hydrogen Electrode Titrations of Benzoic
Acid and Phenol in Ethylenediamine.
(Moss, Elliot and Hall, *Anal. Chem.*, 1948, **20**, 784.)

electrode, show the possibility of titrating mixtures of benzoic
acid and phenol.   Benzoic acid can, of course, be estimated
quite easily in aqueous solution but that is not the case with
phenol.   Another method is seen to be available for the estimation
of amino-acids by the curves in Fig. 110.

Other basic solvents, particularly butylamine, have been used.
Thus Fritz and Lisicki (*Anal. Chem.*,   **23**, 589) found it
to be useful for the titration with the antimony electrode of
weakly acid compounds with sodium methylate dissolved in
methanol and benzene.   Apparently in butylamine the potential
of the glass electrode remains constant throughout titrations so
that it may be used as a reference electrode.   The following have
been titrated in butylamine : acetylacetone, thiophenol, phenol,
nitromethane, carbon dioxide, hydrogen sulphide, sulphur dioxide,
succinimide.   Carbon dioxide must therefore be rigorously
excluded from basic solvent solutions.

Inert solvents such as the alcohols, methanol, ethanol, iso-
propanol and butanol, chloroform, acetonitrile, dioxan and
dimethylformamide, have been used.   Thus Fig. 111 gives the
glass electrode curves of quinine in ethanol and in chloroform

with perchloric acid dissolved in dioxan. Pifer, Wollish and Schmall obtained good inflexions in their curves for the titration of
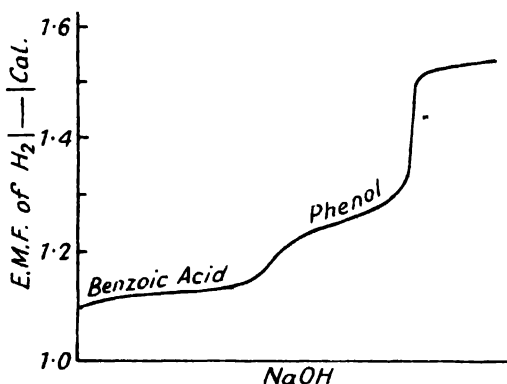

FIG. 109.—Hydrogen Electrode Titration of a mixture
of Benzoic Acid and Phenol in Ethylenediamine.
(Moss, Elliot and Hall, *Anal. Chem.*, 1948, **20**, 784.)

brucine and strychnine with the same titrant.   Wagner, Brown and Peters (*J. Amer. Chem. Soc.*, 1947, **69**, 2611) used the glass electrode
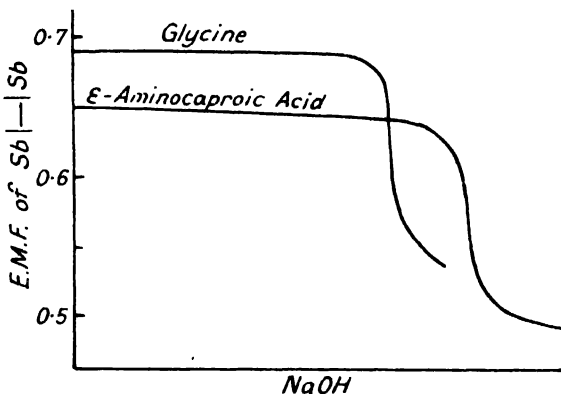

FIG. 110.—Antimony Electrode Titration of Amino-acids
in Ethylenediamine.
(Moss, Elliot and Hall, *Anal. Chem.*, 1948, **20**, 784.)

in methanol solutions of amines which they titrated with 0·5N. hydrochloric acid in isopropylalcohol.   Incidentally they showed that, although it might not always be possible to estimate the amounts of primary and secondary amines present in a mixture by glass electro-titration with a strong acid, owing to the proximity of their respective dissociation constants, advantage can be taken

of the fact that the primary amine can be readily converted into a much weaker base, *viz.*, an azomethine or a so-called Schiff's base,

$$ArCHO + RNH_2 \longrightarrow ArCH{=}NR + H_2O,$$
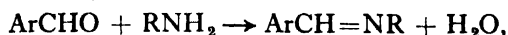
and thus bring about a sufficient difference between the dissociation constants of the remaining secondary amine and the azomethine to produce inflexions showing the two end-points. To form the azomethine, for which purpose they selected salicyl-
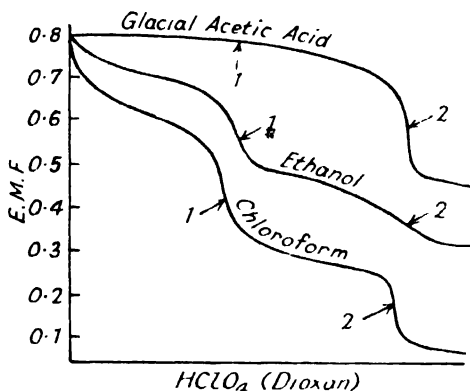

FIG. 111.—Effect of Solvent. Glass Electro-
titrations in the Solvent shown above of Quinine
Base with Perchloric Acid.
(Pifer, Wollish and Schmall, *Anal. Chem.*, 1953, 25,
310.)

aldehyde because of its resistance to air-oxidation, they added 5 c.c. of salicylaldehyde to a solution of about 4 milliequivalents of the primary amine in 80 c.c. of methanol, and after allowing to stand for 30 minutes, proceeded to titrate electrometrically. Curves similar to those in Fig. 112 were obtained.

Acetonitrile has been shown by Fritz (*Anal. Chem.*, 1953, 25, 407) to be an excellent solvent for use with the glass electrode. It is available commercially, but before use he advises that the technical product should be titrated, using the glass electrode, with perchloric acid dissolved in glacial acetic acid and again with perchloric acid dissolved in dioxan in order to be able to assess the magnitude of the errors that may be introduced by the particular sample of acetonitrile used. Small amounts of water in the solvent diminish the sharpness of the end-point inflexions.

Unfortunately, solutions of perchloric acid in acetonitrile are not stable on standing. Instead, Fritz used dioxan solutions of perchloric acid. Whilst in the glacial acetic acid-acetonitrile titration curve for a mixture of butylamine and pyridine, only

one inflexion occurs, *i.e.* corresponding to the two bases, in acetonitrile the neutralisation of the butylamine is indicated by an excellent inflexion and so is the subsequent neutralisation of the pyridine. Pifer and Wollish (Buffalo Meeting, 1952, of the Amer. Chem. Soc.) also obtained two inflexions in their glass electro-titration curve of butylamine and pyridine in dioxan. (Owing to the very low dielectric constant of dioxan and the high resistance of the solution, it is necessary for the glass electrode and the reference electrode to be as close together as possible.)

All titrations in acetonitrile should be performed at ordinary temperature as there is a risk of complications at elevated temperatures. Among other examples illustrating the scope of acetonitrile as a solvent for glass electro-titrations, he gave titration curves of mixtures such as ethanolamine and aniline and butylamine and pyridine, depicted in Fig. 113. Fritz also confirmed the possibility of estimating potentiometrically a primary and secondary amine in the
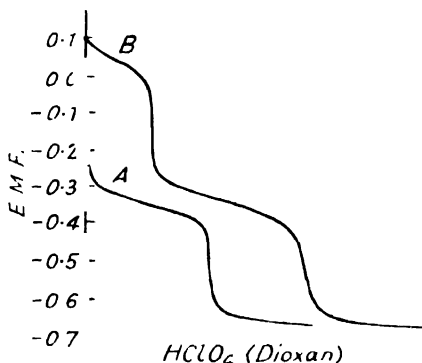

Fig. 112.—Glass Electro-titrations of *A*, Butylamine + Salicylaldehyde ; *B*, Butylamine + Dibutylamine + Salicylaldehyde : in Acetonitrile.

(Fritz, *Anal. Chem.*, 1953, **25**, 407.)

presence of one another as shown by the curves in Fig. 112.

Lykken, Porter, Ruliffson and Tuemmler (*Ind. Eng. Chem., Anal. Edn.*, 1944, **16**, 219) sought a solvent mixture in which they could determine the acids, free and combined, present in highly coloured or opaque materials such as those used with lubricants or lubricants containing oxidation and corrosion inhibitors, detergents, fats and other additives. They found that a mixture of equal volumes of benzene and isopropylalcohol containing from 0·5 to 1 per cent. of water fulfilled their needs.

With such opaque solutes volumetric titration with the aid of coloured indicators is not possible, and in order to apply the potentiometric method to such solutions an electrode had to be chosen that was robust and yielded steady, reproducible potentials. They found the high resistance glass electrode (No. 4990, manufactured by the National Technical Laboratories, U.S.A.) to be suitable, and this was used in conjunction with a sleeve type saturated calomel electrode.

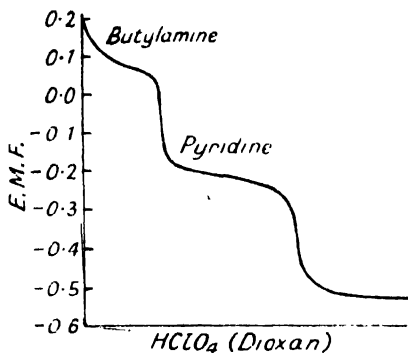To keep the two electrodes in good working order, they were

FIG. 113.—Glass Electro-titration of Bases
in Acetonitrile.
(Fritz, *Anal. Chem.*, 1953, 25, 407.)

rinsed thoroughly with the benzene-isopropylalcohol solvent after each titration, then washed with water, wiped dry and soaked in distilled water until use.

The potentialities 'of this solvent medium may be inferred from Fig. 114 in which, on the left, are titration curves of acids, ranging from the strong acid, hydrochloric acid, to the very weak acid, phenol, and, on the right, are the titration curves of bases of various strengths. The curves for phenol and pyridine represent the limit of the method from the titrimetric standpoint. Owing to their great weakness
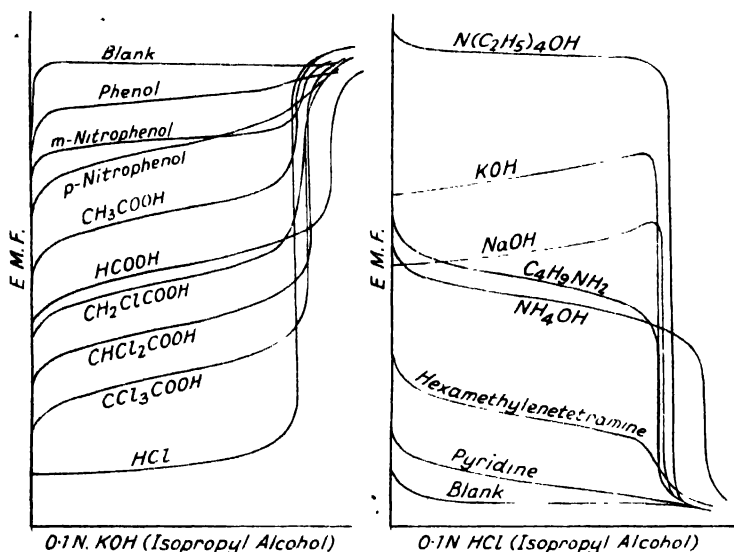

FIG. 114.—Glass Electro-titrations of Acids and Bases in Mixtures of 49·5% Benzene, 49·5% Isopropylalcohol, 1% Water by Volume, with KOH or HCl dissolved in Isopropylalcohol.

(Lykken, Porter, Ruliffson and Tuemmler, *Ind. Eng. Chem., Anal. Edn.*, 1944
16, 219.)

as an acid and a base respectively, the inflexions in their titration curves are so ill-defined as to be of no use quantitatively.

The curves in Fig. 115, representing the titrations of a mixture of hydrochloric acid and acetic acid in different solvents with potassium hydroxide dissolved in isopropylalcohol, show in a striking manner the superiority of the benzene-isopropylalcohol solvent over all the
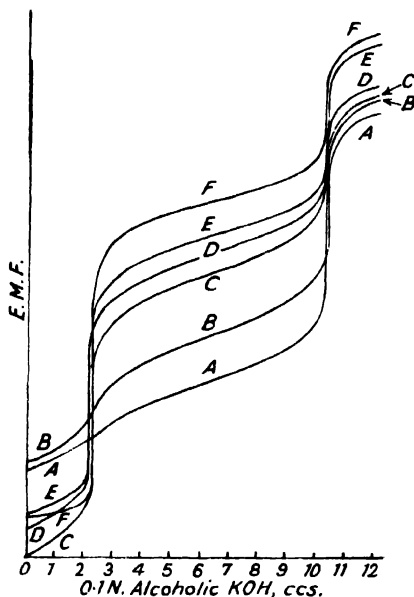

Fig. 115.—Glass Electro-titrations of HCl and CH₃COOH with Alcoholic Potassium Hydroxide in *A*, 125 c.c. of Water ; *B*, 62 c.c. of Methyl Alcohol + 62 c.c. of Water ; *C*, 125 c.c. of Methyl Alcohol (0.5% H_2O) ; *D*, 125 c.c. of Ethyl Alcohol (0.5% H_2O) ; *E*, 125 c.c. of Isopropylalcohol (0.5% H_2O) ; *F*, 62 c.c. of Benzene + 62 c.c. of Isopropylalcohol + 1 c.c of H_2O.
(Lykken, Porter, Ruliffson and Tuemmler, *Ind. Eng. Chem., Anal. Edn.*, 1944, **16**, 219–234.)

others that were employed. As curve *A*, referring to the titration in aqueous solution, shows, the inflexion marking the end of the neutralisation of the hydrochloric acid is very gradual, whereas the corresponding inflexion in curve *F* is extremely well-defined.

Palit (*Ind. Eng. Chem., Anal. Edn.*, 1946, **18**, 246) used, for his glass electrode titrations, mixtures of a solvent which he called " G—H mixtures ". G was any one of the three commercial glycols, *viz.*, the ethylene, propylene and diethylene glycols, and H was either a hydrocarbon or an alcohol or a chlorinated hydrocarbon, etc. Being interested in soaps, he chose the glycols in order to ensure the adequate solvation of molecules such as
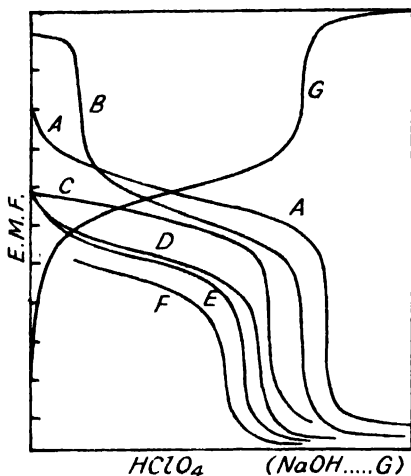
$HClO_4$ $(NaOH.....G)$

FIG. 116.—Glass Electro-titrations in Glycol-Isopropyl Alcohol of various Sodium Salts with an Isopropyl Alcohol Solution of Perchloric Acid, and of Boric Acid with Sodium Hydroxide (Curve *G*): *A*, Sodium Acetate ; *B*, NaOH + Na Cinnamate ; *C*, Borax ; *D*, Sodium Formate ; *E*, Sodium Mandelate ; *F*, Sodium Salicylate.

(Palit, *Ind. Eng. Chem., Anal. Edn.*, 1946, **18**, 246.)

RCOONa in which R is large, whereas H was chosen to provide the requisite solubility. In selecting H the following points were considered : (i) the need for sharp end-point inflexions, (ii) high solvent power, (iii) low viscosity, (iv) low volatility, (v) non-toxicity and (vi) availability. Of the three glycols Palit preferred ethylene glycol, though, he says, the advantages accruing therefrom are not decisive. With salts such as sodium stearate, isopropylalcohol does not confer sufficient solubility so that a more powerful solvent had to be used, *e.g.*, butyl or amyl alcohol, chloroform, dioxan.

The proportion of the volume of isopropylalcohol or other solvent present may extend from 15 to 70 per cent. As a rule, however, a 1 : 1 mixture was used though he says that 20 per cent. by volume of isopropylalcohol is slightly better than 50 per cent. when the sensitivity of the electrode and solubility are considered. As titrant perchloric acid was preferred. In Figs. 116, 117, 118 and 119 are some of the titration curves obtained by Palit. If there existed any parallelism between the pK_a values in water of the acids involved and the E.M.F.s at the mid-points of the replacement reactions in Fig. 116 the initial E.M.F. in the borax titration, C, and the mid-point in the titration curve of boric acid with alkali, G, would have been above that of the mid-point of A. These curves for borax and boric acid are, however, exceptional for curves B, D, E and F are in the order that would be expected from a knowledge of the pK_a values of the respective acids. The apparent strengthening of boric acid with the consequent well-defined inflexion in curve G is most probably due to the formation of a complex glycol-boric acid (*vide*, Boeseken, Vermaas and Kuchlin, *Rec. trav. chim.*, 1930, **49**, 711).

In Figs. 117 and 118 the curves illustrate the remarkable effect which non-aqueous solvents possess in producing inflexions that are greatly superior to those obtained when a salt of a weak acid, or the weak acid itself or a weak base is titrated in an aqueous solution of the same concentration. This effect is even more apparent in Fig. 119, which illustrates the neutralisation of a mixture of sulphuric acid and acetic acid in ethylene glycol-isopropylalcohol solution, in that the two stages of the neutralisation of sulphuric acid are clearly indicated by an inflexion occurring with 1 mol. of NaOH per 1 mol. of H_2SO_4. Such an inflexion is never obtained in aqueous solution.

The antimony electrode has been found by Fritz and Lisicki (*Anal. Chem.*, 1951, 23, 589) to function satisfactorily in a solvent medium consisting of benzene and methanol, which they have used for the titration of *p*-aminobenzoic acid, benzoyl chloride, bromoethylamine hydrobromide, methone (dimethylcyclohexanedione) and strychnine sulphate.

In non-aqueous media, strong acids and bases appear to be much stronger than they are in aqueous solutions and, indeed, differences then become apparent, such as

FIG. 117.—Effect of Solvent. Glass Electro-titration of Sodium Acetate with Perchloric Acid in (a) Water; (b) Mixture of Glycol and Isopropyl Alcohol (50 : 50).

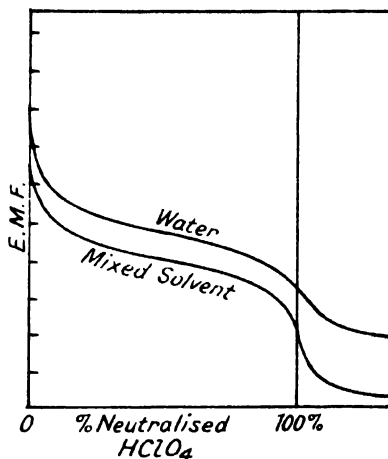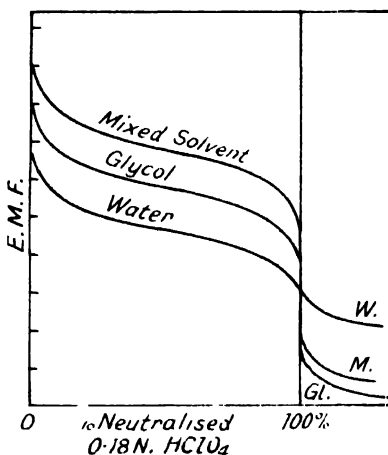(Palit, *Ind. Eng. Chem., Anal. Edn.*, 1946, 18, 246.)

FIG. 118.—Effect of Solvent. Glass Electro-titration of Aniline with Perchloric Acid in (a) Water; (b) Glycol; (c) Mixture of Glycol and Isopropyl Alcohol (50 : 50).

(Palit, *Ind. Eng. Chem., Anal. Edn.*, 1946, 18, 246.) •

that of perchloric acid being an appreciably stronger acid than hydrochloric acid, that are not normally detected in aqueous solution.

Although the potentials, E, that are set up at indicator electrodes, *viz.*, hydrogen, glass, antimony, etc., in non-aqueous solu-
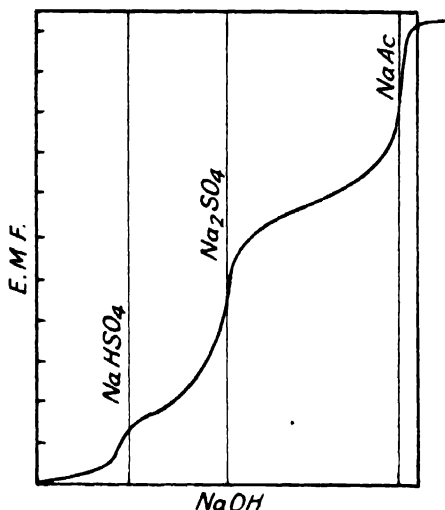

FIG. 119.—Glass Electro-titration of a Glycol-
Isopropyl Alcohol Solution of Sulphuric
Acid and Acetic Acid with Sodium
Hydroxide in Isopropyl Alcohol.
(Palit, *Ind. Eng. Chem., Anal. Edn.*, 1946,
18, 246.)

tions, in which weak acids (or weak bases) are half-neutralised, usually bear something approaching a linear relationship to the pK_a values of the acids (or pK_b of the bases) in aqueous solution, the slope of the line dE/dpK_a is much greater than the theoretical value for aqueous solutions, *viz.*, 59 millivolts at 25° C. per a change of 1 pK_a unit. Thus in the case of weak bases in acetonitrile, dE/dpK_b, Fritz (*loc. cit.*) calculated that 100 millivolts corresponded with a change of 1 pK_b unit. One result of this is that for a small difference in the strengths of two bases a larger inflexion will be produced in a non-aqueous medium than in aqueous solution (see also Lykken *et al.* (*loc. cit.*) for relationship between E in acetonitrile and $pK_{a(water)}$ and Hall (*loc. cit.*) for E for glacial acetic acid and $pK_{b(water)}$).

CHAPTER XXIV

THE FUNDAMENTAL IMPORTANCE OF HYDROGEN-ION CONCENTRATION IN INORGANIC CHEMISTRY. THE PRECIPITATION OF HYDROXIDES

HAVING shown how the hydrogen-ion concentrations set up during the neutralisation of an acid with either a strong base or a weak base, provided that the base is soluble in water, depends upon the dissociation constants of the reactants, we shall now proceed to consider the reactions involving inorganic bases which are insoluble in water. If it were possible to determine the affinity constants of such insoluble bases, then, together with a knowledge of their respective solubility products, it would be possible to place their reactions on a mathematical basis so far as hydrogen-ion con-
centrations were concerned. Nothing, however, of any real value is known of the dissociation constants of insoluble bases, neither can they be calculated with any satisfaction from the hydrolysis constants of their salt solutions by means of the formulæ derived on page 228, Vol. I, for unlike the equilibria there involved these reactions are often heterogeneous as the hydrolysed acid tends to cause the separation of the insoluble base, and though such a separation may not be visible there is every possibility of the base being colloidally dispersed. It is therefore necessary to choose some property which is susceptible to accurate measurement by which the bases can be compared and classified. Measurements of the basic strength by determinations of electromotive force, of heats of formation of oxides and salts, of dissociation pressures of sulphates at different temperatures, and of the hydrolysis of various salts in solution have led to different arrangements. The arrangement in the order of the dissociation constants of the hydroxides as calculated from hydrolysis data is not altogether satisfactory, for in the majority of cases sufficiently accurate measurements cannot be made.

The order of the precipitation of the hydroxides by the gradual addition of alkali has been investigated chiefly by Hildebrand (*J. Amer. Chem. Soc.*, 1913, **35**, 847), Britton (*J. Chem. Soc.*, 1925, **127**, 2110 *et seq.*) and Britton and Robinson (*Trans. Faraday Soc.*, 1932, **28**, 531). A definite hydrogen-ion concentration,

within narrow limits, for those salt concentrations normally employed in analytical procedures has to be attained before the precipitation of any particular hydroxide can take place. This would be expected from a consideration of the "solubility product." An insoluble hydroxide, MOH, attains equilibrium with undissociated molecules and ions in solution, thus :

MOH (solid) $\rightleftharpoons$ MOH (undissociated) $\rightleftharpoons$ M$^\bullet$ + OH'.
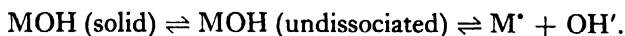
The "solubility product" = [M$^\bullet$][OH'] = [M$^\bullet$]K$_w$/[H$^\bullet$], where K$_w$ = [H$^\bullet$][OH']. The precipitation of the hydroxide thus depends on the concentration of both the metal and the hydrogen ions. In ordinary analytical operations, the concentrations of the metal ions do not vary to any considerable extent and consequently precipitation depends largely on the hydrion concentration. The hydrion concentrations necessary for the precipitation of a large number of hydroxides, which have now been determined, constitute a suitable basis for the classification of the hydroxides. The order is "parallel" with the increasing magnitude of the solubility products, but whether it is that of the basic strengths cannot be stated with certainty ; this can be so only if the concentration of undissociated molecules is the same for each hydroxide—a point about which nothing is known.

Effect of Concentration, Anion, and Precipitant on the Hydrogen-Ion Concentrations required for the Precipitation of Hydroxides.

The precipitation pH of a metallic hydroxide is usually almost unaffected by the acid radicals, sulphate, nitrate and chloride, although both nitrate and chloride tend to delay the actual separation of precipitates ; tending to maintain the basic precipitates in a state of colloidal dispersion. Owing to great tendency of organic acids, $e.g.$, acetic and tartaric, to enter into complex formation with metallic bases, alkalis may not yield precipitates until considerably higher pH values are reached. In some cases, precipitation is prevented altogether.

In the case of alkali precipitation from mercuric salt solutions, the anion is, however, of vital importance as illustrated in Fig. 130 Owing to the ease with which divalent mercury enters into complex formation, the pH at which precipitation occurs is greatly influenced by neutral salts. Table 163 gives the pH values at which thorium hydroxide begins to be precipitated by N/10-sodium hydroxide at 15° from solutions of thorium nitrate ranging in concentration from M./1000 to M./100.

TABLE 163

EFFECT OF CONCENTRATION ON PRECIPITATION *p*H OF
THORIUM HYDROXIDE

Concentration.	*p*H.
0·001 M.	3·60
0·002 M.	3·58
0·01 M.	3·57

The difference in *p*H is thus very small and this range of concentrations covers those usually employed in analytical work. The differences in the *p*H values of precipitation from solutions of different salt concentrations are usually greater than with thorium hydroxide. The reason undoubtedly lies in the quadrivalency of thorium, for any small variation in the Th''''-ion concentration of a solution will theoretically impose a quarter of that variation on the hydroxyl-ion concentration to maintain the constancy of the solubility product, [Th''''][OH']^4. Variation in the concentration of metallic salt of lower valency has a greater effect on the *p*H at which the hydroxide is precipitated than is the case with thorium salt solutions. Such effects are shown in Fig. 122 in the case of the precipitation of silver oxide, zinc hydroxide and copper hydroxide from solutions of different concentrations. As we shall see later, metallic hydroxides are scarcely ever precipitated as such, but only in conjunction with some undecomposed salt in the form of a basic salt.

The effect of the anion and of the basic nature of the precipitant is shown in Fig. 120 in connexion with various thorium salt solutions. Precipitation began at the same *p*H in every case.

Curves 1, 2, and 3 represent the titrations of 100 c.c. of M./100-solutions of thorium nitrate, chloride, and sulphate respectively, with 0·1016 N-sodium hydroxide, and curve 4 that of 100 c.c. of M. 100-thorium nitrate with 0·1115 N-ammonium hydroxide, at 15°. The commencement of precipitation, *i.e.*, the first appearance of turbidity, is shown by arrows.

Appreciable amounts of alkali had to be added before the commencement of precipitation, and thereafter, in the case of the nitrate and the chloride solutions, there was a distinct tendency for a constant *p*H to be maintained during the addition of the greater portion of the alkali. It is probable that this corresponds to the separation of a precipitate of uniform composition.

In neither case was thorium hydroxide precipitated as such. Fig. 120 shows that precipitation was complete and the mother-

liquors had become alkaline some time before the stoicheiometrical quantities of alkali had been added. The following table gives the amounts of alkali which were added before precipitation ensued and the amounts of alkali which had to be added before the solutions became neutral (pH 7).
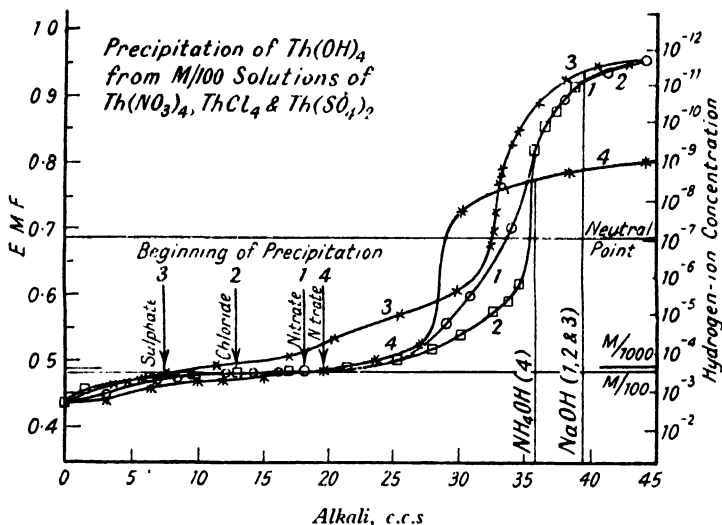

FIG.120.—Precipitations from Thorium Salt Solutions with Alkalis, followed by the Hydrogen Electrode, compared with the Normal Calomel Electrode.

TABLE 164

EFFECT OF ANION AND PRECIPITANT ON THE PRECIPITATION OF THORIA

Curve.	Solution and Precipitant.	Precipitation began		Equivs. of Alkali required for Neutrality.	Composition of Precipitate.
		pH	Equivs. of Alkali.		
1	Th(NO$_3$)$_4$ and NaOH	3·57	1·85	3·43	Th(OH)$_{3\cdot43}$(NO$_3$)$_{0\cdot75}$
2	ThCl$_4$ and NaOH	3·51	1·30	3·58	Th(OH)$_{3\cdot58}$Cl$_{0\cdot42}$
3	Th(SO$_4$)$_2$ and NaOH	3·53	0·78	3·31	Th(OH)$_{3\cdot31}$(SO$_4$)$_{0\cdot35}$
4	Th(NO$_3$)$_4$ and NH$_4$OH	3·57	2·21	3·24	Th(OH)$_{3\cdot24}$(NO$_3$)$_{0\cdot76}$

The last two columns of the above table show that the precipitate formed in each titration was basic, being somewhat less so when the precipitant was ammonium hydroxide. The protracted inflexions produced during the last stages of precipitation show that the precipitates at first formed were less basic and suffered some decomposition on further addition of alkali. This seems to have taken place readily in the cases of the nitrate and the chloride, but the slowness with which apparent equilibrium was attained

in the second part of the sulphate titration indicates that the basic sulphate was undergoing hydrolysis with much greater difficulty. It seems almost unnecessary to say that the amounts of acid radical retained by these precipitates were too great to be accounted for by adsorption from such dilute solutions. These precipitates were not completely decomposed even when excess of alkali was added. It is also an interesting fact that the sulphate radical tends to form more stable basic salts than do other acid radicals, and this is true of the basic micelles present in solutions like zirconium sulphate solutions. The basic sulphates exercise a peculiar effect on their chemical properties of the metals concerned (see p. 60).

Another remarkable fact arising from these titrations is that alkali ranging in amounts from 0·78 to 2·21 equivalents to one molecule of thorium salt had to be added before the appearance of a precipitate. These amounts, which vary with the nature of the anion and the precipitant, do not permit of a guess as to the way in which the thorium hydroxide, or basic complex, is held in solution until the attainment of the *p*H requisite for precipitation. According to Ordway (*Amer. J. Sci.*, 1858, **26**, 197), Berzelius observed that when alkali was added to a thorium sulphate solution precipitation was delayed owing t ∂ the formation of what appeared to be *un soussel soluble*. Ordway directed attention to several other examples of " soluble basic salt " formation. It will be shown in the course of the following chapters that these so-called soluble basic salts exert a pronounced influence on some of the reactions of the metals of which they are characteristic. It is surprising that " soluble basic salts " are generally formed by those metals the valencies of which are greater than two, although this is not the case with the tervalent rare-earths. Bivalent beryllium has, however, the remarkable property of forming these basic solutions.

The Precipitation of the Hydroxides of Magnesium, Manganese, Cobalt, Nickel, and Ferrous Iron.—The following table gives particulars of the solutions used in typical titrations, together with the amount of alkali required to cause incipient precipitation. The courses of the titrations are shown in Fig. 121.

In contrast with the thorium salt titrations, the first few drops of sodium hydroxide caused a rapid diminution in hydrion concentration until a value was obtained at which precipitation commenced. Thereafter, precipitation proceeded with very little change in *p*H until the separation was nearly complete. The titration of ferrous sulphate solutions was a matter of some difficulty. As is well known, manganous and ferrous hydroxides on exposure to air readily become oxidised, and consequently the titrations

involving their precipitation were performed in vessels which were stoppered as far as possible. Even so, it was not possible to prevent some oxidation from taking place, although plenty of hydrogen was passing through the solutions.
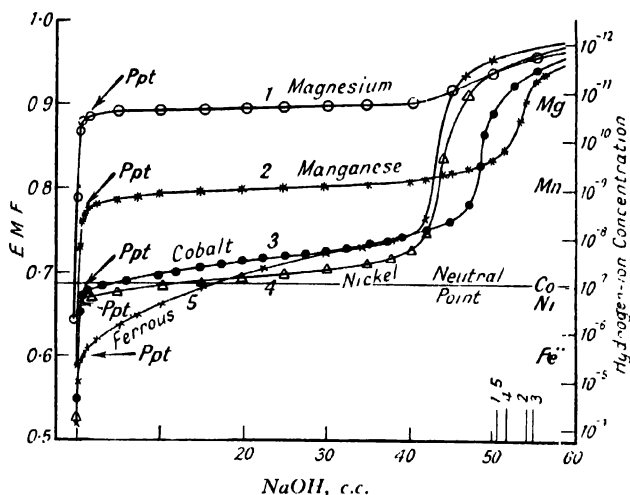

FIG. 121.—Precipitations followed by the Hydrogen Electrode (against the Normal Calomel Electrode).

TABLE 165

PRECIPITATION OF HYDROXIDES (FIG. 121)

Titration and Curve No.	Solution Titrated. 100 c c.	Normality of NaOH.	C c of NaOH theoretically required.	Precipitation first began. pH.	Precipitation first began. C.c. of NaOH	Precipitation ended Equivs NaOH
1	0 025 M.-MgSO₄	0·0990	50·5	10·49	1·6	1·64
2	0·024 M.-MnCl₂	0·0900	54·0	8·41	1·0	1·93
3	0·0247 M.-CoCl₂	0·0900	54·8	6·81	0·9	1·75
4	0·025 M.-NiCl₂	0·0967	51·7	6·66	0·6	1·66
5	0·025 M.-FeSO₄	0·0990	50·5	5·49	0·8	1·71

Precipitation was again complete in each case some time before the theoretical amount of alkali·had been added. Curve No. 1, magnesium sulphate, shows that the final inflexion began when 1·64 equivalents of sodium hydroxide had been added. The gradual slope of the inflexion was evidently due to the partial decomposition of the basic sulphate, originally precipitated. A similar inflexion, but steeper, took place in magnesium chloride titrations. Hildebrand and Harned (*Orig. Com. 8th Inter. Cong. Appl. Chem.*, 1912, 1, 217) and Hildebrand (*J. Amer. Chem. Soc.*,

1913, **35**, 847) have also studied by means of the hydrogen electrode the precipitation of magnesium hydroxide and have suggested that the electrometric titration of hydrochloric acid solutions of dolomite might be used for the estimation of the magnesia with an accuracy of about 1 per cent., despite the fact that the values obtained by them showed a variation of 5 per cent. The difficulty is that magnesium hydroxide is not precipitated simply from either chloride or sulphate solutions to give sharp inflexions, but indefinite basic precipitates are formed which give poorly defined inflexions ; this renders it impossible to assign a point on the curve which exactly corresponds to the neutralisation of all the acid which was originally combined with the magnesium hydroxide. According to Kolthoff (*Rec. trav. chim.*, 1922, **41**, 787), Pinkof (*Thesis*, Amsterdam, 1919, p. 34) has investigated the electrometric estimation of magnesia by means of the Hg|HgO Alkali electrode, but obtained unsatisfactory inflexions, even when an excess of alkali was added and the free alkali afterwards titrated. Kolthoff recommended shaking the magnesium salt solution with an excess of alkali and allowing to stand so as to render the decomposition of the basic salts as complete as possible before titration.

Calculation of Solubility Products.

In the majority of alkali precipitations, the hydroxide of the metal, as such, is not precipitated. Instead, a basic salt containing some unattacked metal salt is formed. The composition of such basic precipitates often depends on the rate at which the alkali is added ; slow addition usually producing a less basic salt. In certain precipitations, the composition of the precipitates varies progressively and the precipitates become increasingly basic as more and more alkali is added. Even though the hydroxides are not ordinarily precipitated, calculations of " solubility products " prevailing during the course of precipitation justify the belief that the separation of hydroxides is the chief determining factor in causing precipitation.

In order to calculate approximately the " solubility product " of the metal hydroxide involved in such a precipitation, it is assumed that the composition of the basic salt is that indicated by the position of the final inflexion in the *p*H curve and that this composition remains fixed throughout the whole course of precipitation. As stated above, this is rarely the case,' but any discrepancies introduced by making such an assumption will not be considerable. The assumption makes it possible to calculate the concentration of metallic salt remaining in solution when any volume of alkali solution is added. It thus becomes possible to

calculate the concentration of metal ions at any stage during precipitation, whilst the concentration of hydroxyl ions can be computed from the pH and K_w.

Tables 166, 167 and 168 illustrate the results of such calculations, based on titrations with either the hydrogen, glass or quinhydrone electrodes (Britton and Robinson, *Trans. Faraday Soc.*, 1932, **28**, 531).

<div align="center">

TABLE 166

PRECIPITATION OF SILVER HYDROXIDE FROM SILVER NITRATE
SOLUTION

</div>

Equiv. NaOH	0 1.	0 2.	0 3.	0 4.	0 5.	0 6.	0 7	0 8.	0·9.
1. 100 c.c. 0·100 M.-AgNO₃ with 0·2 N-NaOH.									
pH . . .	7·48	7·54	7·61	7·69	7·81	7·92	8·03	8·21	8·56
L × 10⁸ . .	1·62	1·58	1·55	1·55	1·62	1·62	1·51	1·45	1·58
L_c × 10⁸ . .	1·34	1·32	1·32	1·32	1·43	1·46	1·38	1·34	1·50
2. 100 c.c. 0·025 M.-AgNO₃ with 0·2 N-NaOH.									
pH . . .	7·97	8·04	8·11	8·17	8·25	8·34	8·49	8·70	9·04
L × 10⁸ . .	1·32	1·35	1·38	1·33	1·30	1·29	1·34	1·44	1·58
L_c × 10⁸ . .	1·19	1·22	1·26	1·22	1·21	1·20	1·26	1·37	1·52

In the calculations referring to titrations 1a and 1b, Table 167, it was assumed that no magnesium sulphate was entrained by the precipitates. The fact that some was carried down is not markedly reflected in the inflexion of the glass electrode curve in Fig. 122. The values of L remained remarkably constant, although the mean value given by the hydrogen electrode curve was $1·3 \times 10^{-9}$, whereas that given by the glass electrode titration was slightly higher, *viz.*, $2·2 \times 10^{-9}$. With the possible exceptions of nickel, copper, and lead, the solubility products show no constancy but increase with the amount of alkali added. This is very pronounced in the cases of $[Fe^{..}][OH']^2$, the value of which rapidly increased from 9×10^{-19} to 1×10^{-15}, and of $[Pb^{..}][OH']^2$, which ranges from 3×10^{-19} to $1·35 \times 10^{-15}$.

Similarly in the zinc salt solutions (Table 168) it is seen that the solubility product principle is not obeyed, at any rate when applied to the zinc and hydroxyl ions. Kolthoff and Kameda (*J. Amer. Chem. Soc.*, 1931, **53**, 832) calculated the value of $[Zn^{..}][OH']^2$ to be 1×10^{-17}, using the pH value prevailing at the point of initial precipitation in zinc sulphate solution, whilst Prytz (*Z. anorg. Chem.*, 1931, **200**, 133) from the pH value set up when one equivalent of alkali had been added to a zinc chloride solution gave the value $1·29 \times 10^{-17}$.

The value of $[Mg^{\cdot\cdot}][OH']^2$ is usually considered to be $3\cdot4 \times 10^{-11}$ at $18°$ as indicated by the conductivity measurements of Kohlrausch and Rose (*Z. physikal. Chem.*, 1893, **12**, 241).
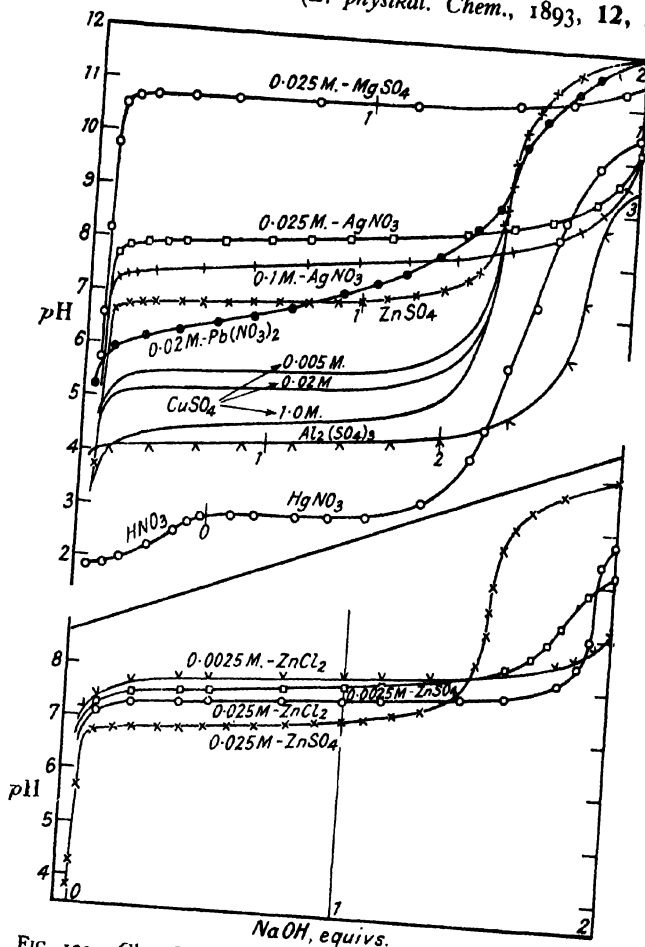

FIG. 122.—Glass Electrode Titrations involving Precipitations.

The values now obtained are very much larger. A perusal of the solubility figures given for magnesium oxide obtained by direct analysis, shows a wide variation in the recorded values. The data of Fresenius, however, lead to $1\cdot35 \times 10^{-9}$, which is similar to that obtained by the authors.

TABLE 167

PRECIPITATION OF BASIC SALTS

Equivs. NaOH.	0 1.	0 25.	0 5.	0 75.	1 0.	1 25.	1 5.	1 75
Magnesium.	Hydrogen electrode : 100 c.c. 0·025 M.-MgSO₄ with 0·099 N.-NaOH.							
1*a*.	pH 10·57 $L \times 10^9$ 1·3	10·64 1·6	10·67 1·4	10·69 1·3	10·75 1·2	10·80 1·1	10·86 1·0	11·12 1·5
1*b*.	Glass electrode : 100 c.c. 0·025 M.-MgSO₄ with 0·1 N-NaOH.							
	pH 10·69 $L \times 10^9$ 2·2	10·70 2·3	10·75 2·2	10·80 2·3	10·86 2·3	10·90 2·3	11·00 2·4	11·13 1·8
Manganese.	Hydrogen electrode : 100 c.c. 0·024 M.-MnCl₂ with 0·090 N-NaOH.							
2.	pH 8·63 $L \times 10^{13}$ 2·3	8·76 3·7	8·90 5·8	8·99 6·9	9·03 6·6	9·05 5·7	9·11 4·8	9·37 9·1
Cobalt.	Hydrogen electrode : 100 c.c. 0·0247 M.-CoCl₂ with 0·090 N-NaOH.							
3.	pH 6·95 $L \times 10^{16}$ 1·0	7·07 1·5	7·29 3·2	7·50 6·5	7·64 8·7	7·80 11·5	8·09 20·9	— —
Nickel.	Hydrogen electrode : 100 c.c. 0·025 M.-NiCl₂ with 0·0967 N-NaOH.							
4.	pH 6·76 $L \times 10^{16}$ 0·3	6·92 0·6	7·04 0·9	7·13 1·0	7·30 1·5	7·46 1·8	7·69 1·9	— —
Ferrous.	Hydrogen electrode : 100 c.c. 0·025 M.-FeSO₄ with 0·099 N-NaOH.							
5.	pH 5·93 $L \times 10^{17}$ 0·09	6·28 0·4	6·78 3·1	7·18 15	7 47 40	7·72 78	7·95 100	— —
Lead.	Quinhydrone electrode : 100 c.c. 0·005 M.-Pb(NO₃)₂ with 0·1 N-NaOH.							
6.	pH 6·00 $L \times 10^{17}$ 0·03	6·60 0·4	— —	6 80 0·5	7·26 2·9	7·75 135	— —	— —
Copper.	Quinhydrone electrode : 100 c.c. 0·005 M.-CuSO₄ with 0·1 N-NaOH.							
7.	pH 5·37 $L \times 10^{20}$ 1·4	5·40 1·4	— —	5·47 1·2	5·56 1·2	5·74 13	— —	— —
Aluminium.	Glass electrode : 100 c.c. 0·00343 M.-Al₂(SO₄)₃ with 0·194 N-NaOH.							
8.	pH — $L \times 10^{32}$ —	4·17 0·5	4·23 0·7	4·28 0·8	4·32 1·0	4·37 1·2	4·43 1·5	4·52 2 1
	2·0 equivs. pH 4·61. L 3·0 × 10³².							
	2·25 ,, pH 4·81. L 8·0 × 10³².							

Equivs. NaOH for complete precipitation :
2. 0·93. 3. 1·75. 4. 1·66. 5. 1·71. 6. 1·5. 7 1·5. 8. 2·73.

TABLE 168

PRECIPITATION BY SODIUM HYDROXIDE FROM ZINC SALT SOLUTIONS

Equivs. NaOH.	0 1.	0 2.	0 4.	0 6.	0 8.	1 0.	1 2.	1·4.	1·6.	1 8.
1. 100 c.c. 0·025 M.-ZnSO$_4$ with 0·1 N-NaOH.										
pH	6·77	6·83	6·89	6·96	7·04	7·17	7·30	7·71	—	—
L × 10^{17}	3·2	3·8	4·0	4·4	4·8	6·0	6·6	17	—	—
2. 100 c.c. 0·0025 M.-ZnSO$_4$ with 0·01 N-NaOH.										
pH	7·36	7·41	7·56	7·63	7·755	7·88	7·98	8·11	8·31	—
L × 10^{17}	4·8	5·6	9·3	10·5	14·8	20·9	24·0	28·2	36·3	—
3. 100 c.c. 0·01 N-HCl, 0·025 M.-ZnCl$_2$ with 0·2 N-NaOH.										
pH	7·13	7·24	7·38	7·42	7·49	7·57	7·62	7·72	7·82	8·15
L × 10^{17}	17·0	25·1	41·7	42·7	49·0	58·9	57·5	67·6	69·2	155
4. 100 c.c. 0·001 N-HCl, 0·0025 M.-ZnCl$_2$ with 0·02 N-NaOH.										
pH	7·45	7·60	7·74	7·84	7·92	8·00	8·06	8·13	8·26	8·42
L × 10^{17}	6·9	13·2	21·9	29·5	35·5	42·7	43·7	44·7	52·5	53·7

Applebey and Reid (*J. Chem. Soc.*, 1922, **121**, 2129) give figures for [Pb$^{..}$][OH$'$]^2 based on the potentials of lead electrodes immersed in sodium hydroxide solutions saturated with various forms of lead monoxide. Thus at 20° they obtained 4·7 × 10^{-18} and 9·1 × 10^{-16}. Table 167, however, shows that very different values hold during the basic precipitation of a lead nitrate solution.

Randall and Frandsen (*J. Amer. Chem. Soc.*, 1932, **54**, 46) have summarised the various published values of [Fe$^{..}$][OH$'$]^2. They range from 1·6 × 10^{-19} to 1·6 × 10^{-14}. Table 130 shows that the values for the different stages of the precipitation of basic ferrous sulphate ranged from 9 × 10^{-19} to 1 × 10^{-15}. Kriukov and Awsejewitch (*Z. Elektrochem.*, 1933, **39**, 890), taking considerable precautions to prevent any possibility of ferrous hydroxide being oxidised by the air, found that precipitation occurred from 0·05 M.-FeSO$_4$ between pH 7·68 and pH 8·97, and showed, using the same assumptions made here, that [Fe$^{..}$][OH$'$]^2 ranged from 3·2 × 10^{-15} at the beginning to 6·8 × 10^{-14} at the end of the titration.

Kriukov and Awsejewitch also determined the pH of precipitation from ferric sulphate with sodium hydroxide which lay between 2·3 and 3·7 (*cf.* oxygen electrode curve, Fig. 128). An approximate calculation by Britton (*J. Chem. Soc.*, 1925, **127**,

2156) revealed that at the incidence of precipitation from ferric chloride $[Fe^{\cdots}][OH']^3 = 10^{-37.7}$, whereas the above authors' values ranged from 1×10^{37} to 2.2×10^{-13} as precipitation proceeded.

Bennett (*J. Physical Chem.*, 1934, **38**, 573) has shown that during the precipitation of the basic nitrate, apparently $3Hg_2O,2HgNO_3$, from mercurous nitrate solution, $[Hg_2^{\cdot\cdot}][OH']^2$ ranged from 2·0 to 14.9×10^{24}, giving an average value of 7.8×10^{24} (*cf.* 1.82×10^{24}, Bugarsky, *Z. anorg. Chem.*, 1897, **14**, 146; 8.05×10^{24}, Immerwahr, *Z. Elektrochem.*, 1907, **7**, 477; 4.8×10^{24}, Allmand, *ibid.*, 1910, **16**, 263).

Fig. 122, which gives curves obtained by Britton and Robinson (*loc. cit.*), shows that the inflexions were obtained when the stoicheiometrical amounts of alkali were added to precipitate silver hydroxide completely. The values of L in Table 166 were calculated by neglecting the degree of ionisation of silver nitrate remaining in solution, whereas L_c represents the actual ionic product, $[Ag^{\cdot}][OH']$, the $[Ag^{\cdot}]$ being considered equal to $\alpha \times C_{AgNO_3}$. The appropriate values of α were found from the conductivity data of Kohlrausch and Steinwehr (*Sitzber. Berlin Akad.*, 1902, 581). It might perhaps be considered a more satisfactory procedure to express the solubility product, $[Ag^{\cdot}][OH']$, in terms of " activities," thus

$$a_{Ag} \cdot a_{OH} = \gamma_{Ag} \cdot [Ag^{\cdot}] \cdot a_{OH} = \gamma_{Ag} \cdot [Ag^{\cdot}]K_w/a_H.$$

Since the glass electrode depends for its calibration on a hydrogen electrode titration of a universal buffer mixture, and consequently *if it can be assumed that the liquid junction potentials are eliminated by the use of a saturated potassium nitrate salt-bridge*, the values given by both the hydrogen and glass electrodes are, strictly speaking, hydrogen-ion activities rather than hydrogen-ion concentrations. Moreover, as during the entire precipitation process the total ionic concentration remained constant there occurred but little variation in the activity coefficient of the silver ion. According to Lewis and Randall (" Thermodynamics," 1923, p. 362) its value in N/10 solution is 0/732 and in N/40 solution 0·840. Applying these factors to the mean solubility products given in Table 166, values of 1.14×10^{-8} and 1.13×10^{-8} respectively are obtained.

A number of determinations of the solubility product have been made by conductivity, silver electrode and analytical methods. The following table summarises the more reliable values of the solubility product of silver hydroxide.

SOLUBILITY PRODUCT OF SILVER HYDROXIDE

[Ag'][OH'] × 10⁸.	Observer.	Method.	Temp.
0·9	Abegg and Cox	Silver electrode	25°
1·33	Britton and Robinson	Glass electrode	16°
1·50	Britton	Silver electrode	20°
1·52	Böttger	Conductivity	20°
1·93	Böttger	Conductivity	25°
2·25	Noyes and Kohr	Equilibria	25°
2·2–3·4	Whitby	Analysis	20°
3·0–5·1	Noyes and Kohr	Analysis	25°

If the solubility products of metallic hydroxides are to have any real significance, it is essential that they should have direct bearing on the ionic concentrations prevailing during their precipitation. With the exception of silver hydroxide, it is by no means certain that any such relationship exists. From the results given in Tables 167 and 168, it would appear that the solubility product principle as applied to the metallic ions and hydroxyl ions alone cannot be applied, except in a roughly approximate sense, to the alkali precipitation of basic salts.

Use of Ammonium Chloride in Analysis.

These alkali precipitation curves throw considerable light on the function of ammonium salts in preventing the precipitation of certain hydroxides. The addition of ammonium salts to ammonia may be such that the *p*H is depressed below the precipitation value of either magnesium or manganous hydroxide. The approximate hydrogen-ion concentration of a solution containing ammonium hydroxide and ammonium chloride is given by

$$[H'] = \frac{[NH_4Cl]K_w}{[NH_4OH]K_{NH_4OH}},$$

where $K_w = 10^{-14.14}$ and $K_{NH_4OH} = 10^{-4.64}$ at 18°.

If ammonium chloride is regarded as being completely dissociated, the minimum number of molecules of ammonium chloride to be added to each molecule of ammonia to increase the hydrion concentration to that required just to start precipitation of (*a*) magnesium hydroxide is 0·08, (*b*) manganous hydroxide, 4·5, (*c*) cobaltous hydroxide, 380, and (*d*) hydroxides of nickel, zinc and ferrous iron, still more. In analytical processes, the condition for the prevention of the precipitation of the hydroxides of magnesium and manganese is easily satisfied, but the sole cause of the partial or non-precipitation of the other hydroxides

is the appreciable quantities of ammonium chloride that must be present. Herz (*Z. anorg. Chem.*, 1900, **23**, 227) stated that ammonium chloride in depressing the hydroxyl-ion concentration was the cause of the non-precipitation of zinc hydroxide. Although ammonium chloride has undoubtedly some influence, it is the ammonia which is chiefly responsible for the maintenance of the hydroxides of zinc, cobalt, and nickel in solution through the formation of complex ions. The researches of Lovén (*loc. cit.*), Treadwell (*Z. anorg. Chem.*, 1903, **37**, 326), and Herz and Muhs (*ibid.*, 1904, **38**, 138) have all led to the conclusion, given more directly by these magnesium precipitation curves, regarding the influence of ammonium salts in preventing the precipitation of magnesium hydroxide. There are no grounds for attributing it to the formation of a complex magnesium anion— an explanation which is still to be found in some text-books.

The Precipitation and the so-called Amphoteric Nature of the Hydroxides of Zinc, Chromium, Beryllium, Aluminium, Bivalent Tin, and Zirconium.

Those hydroxides, including zirconium hydroxide, which are generally supposed to have both basic and acidic properties, will now be considered, first with respect to their precipitation, and secondly with respect to the changes in hydrion concentration produced when they react with sodium hydroxide in various proportions. It is very doubtful whether zirconium hydroxide is amphoteric ; Hildebrand (*J. Amer. Chem. Soc.*, 1913, **35**, 847), however, has obtained electrometric evidence for the existence of zirconates.

Aluminium and Beryllium Hydroxides.

We shall, in the first place, consider the amphoteric nature of aluminium and beryllium hydroxides, and shall therefore direct our attention to the hydrogen electrode curves given in Figs. 123 and 124 ; the particulars of the solutions titrated being given in Table 170 (Britton, *J. Chem. Soc.*, 1925, **127**, 2121 ; 1927, 422).

Aluminium.

The aluminium sulphate curves in Figs. 123 and 124 show that precipitates did not visibly begin to form until somewhat over 0·3 equiv. of alkali had been added, and when the same pH had been reached, *viz.*, pH 4·1. In the aluminium chloride reactions with strontia and baryta the solutions remained clear until 2·09 equivs., pH 4·76, and 1·92 equivs., pH 4·69, respectively, of alkali had been added ; opalescence only was then produced, coagulation of the precipitates not occurring until 2·71 and 2·88

TABLE 170

Solution 100 c c of —	Titrated with—	Precipitation began at —		Precipitate Dissolved at—	
		*p*H.	Equivs. Alkali per 1 Al	*p*H.	Equivs. Alkali per 1 Al.
0·00667 M.-Al$_2$(SO$_4$)$_3$	0·090 N-NaOH	4·14	0·35	10·8	4·13
0·00349 M.-Al$_2$(SO$_4$)$_3$	0·0447 N-Ca(OH)$_2$	4·14	0·32	10·2	3·90
0·00333 M.-AlCl$_3$	0·0558 N-Ba(OH)$_2$	Opalescent 4·76	2·09	—	—
,,	,,	Coagulated 6·50	2·71	10·4	4·02
0·00408 M.-AlCl$_3$	0·0391 N-Sr(OH)$_2$	Opalescent 4·69	1·92	—	—
,,	,,	Coagulated 6·50	2·88	10·6	4·02
0·02 M.-BeSO$_4$	0·090 N-NaOH	5·69	1·04 (to 1 Be)	—	—

equivs., respectively, had been added, and a considerably higher *p*H attained, *viz.*, 6·5. This delay in precipitation, despite the fact that the requisite precipitation, *p*H 4·14, had been exceeded, and that nearly the total stoicheiometrical quantity of alkali had been added, is due to the characteristic tendency of chlorides to promote the formation of colloidal solutions—the dispersed particles formed in the initial stage of the reactions being too small to affect the appearance of the solution to the unaided eye. A similar instance is that of the chloride and sulphate of zirconium (Britton, *J. Chem. Soc.*, 1925, **127**, 2125). In the case of the titration represented in Fig. 123 precipitation did not begin until the dissolved aluminium sulphate had acquired the composition Al$_2$O$_3$,2·65SO$_3$, and was complete when 2·85 equivalents had been added, thereby showing that the basic precipitate contained Al$_2$O$_3$,0·15SO$_3$. Williamson (*J. Physical Chem.*, 1923, **27**, 284) found that the precipitates formed by the addition of 1 to 2 equivalents of sodium hydroxide were of nearly constant composition and approximated to Al$_2$O$_3$,0·6SO$_3$,3H$_2$O. Miller (*U.S. Public Health Reports*, 1923, **38**, 1995) found that the greatest insolubility of the precipitate occurred when 2·75 equivalents of sodium hydroxide had been added and a hydrion concentration between 10$^{-6\cdot7}$ and 10^{-7} had been reached. This state corresponds to the maximum decomposition of the basic sulphate which was first precipitated.

The solutions became neutral when the sodium hydroxide and the alkaline earths had been added in amounts slightly less than
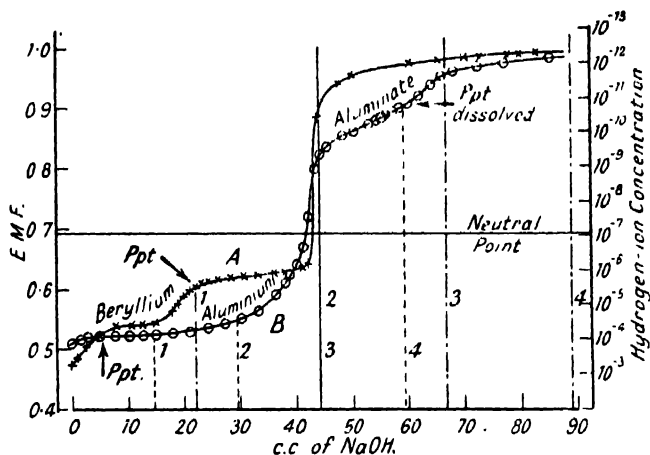
FIG. 123.—Hydrogen Electrode Precipitation Curves, showing Amphoteric Nature of Aluminium Hydroxide.
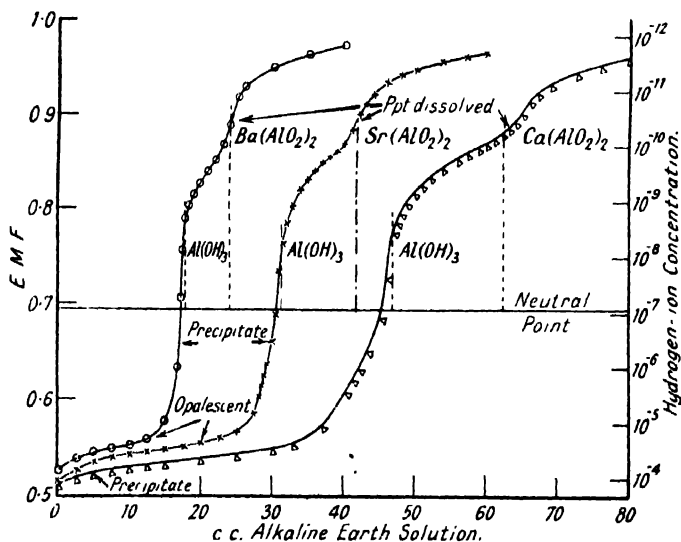
FIG. 124.—Amphoteric Nature of Aluminium Hydroxide

those required for the formation of aluminium hydroxide owing
to the retention by the precipitates of some of the acid radical
present in the original salts.   In each of the titrations, the precipi-
tates redissolved completely when approximately another equiva-
lent of alkaline earth had been added, the dissolutions being
reflected in the characteristic aluminate inflexions of the titration
curves extending over a *p*H range from 8 to 10·5.   Magistad's
(*Soil Science*, 1925, **20**, 181) results on the solubility of alumina in
sodium hydroxide solutions of varying *p*H are important in that
they show that the solubility first becomes perceptible at *p*H 7·55,
being then 2 parts per million ; at *p*H 8·35, the solubility is 8·4
parts, but thereafter it increases rapidly to 34·6 parts per million
at *p*H 8·95.   Hence, it appears probable that the formulæ $M^I AlO_2$
and $M^{II}(AlO_2)_2$ represent the condition in which aluminium
hydroxide exists in solutions of the hydroxides of the alkali- and
alkaline-earth metals respectively.   In no other instance of the
so-called amphoteric hydroxides is such an inflexion produced.
Incidentally, in all cases the amounts of alkali required to dissolve
the hydroxides, except that of zirconium, which does not dissolve,
are considerably in excess of that denoted by the formulæ of the
salts which have been said to be formed.   In the case of aluminium
hydroxide only is the amount of alkali required for its re-solution
approximately equal to that suggested by the formula $NaAlO_2$, and
is also independent of the concentration of the sodium hydroxide
used (compare Britton, *Analyst*, 1921, **46**, 363).   It is possible
that the other hydroxides may be acidic in their behaviour towards
alkalis, but to so small an extent that the hydrogen-ion concen-
tration of the alkali solution is scarcely affected.

It should be mentioned that in the calcium hydroxide titration
a fine precipitate containing both calcium and aluminium began to
separate at *p*H 11·7 when 90 c.c. of lime-water had been added.
It follows, therefore, that the disappearance of alumina from " soil
solutions " cannot be attributed, as Marais (*Soil Science*, 1922,
13, 368) states, to the formation of an insoluble calcium aluminate,
for the hydrogen-ion concentration of ordinary " soil solutions "
never becomes so low as *p*H 11·7.   Wells (*U.S. Bur. Stand. Res.
Paper*, No. 34, 1928) has studied the action of water on calcium
aluminate cements from the standpoint of the *p*H values prevailing
during the initial dissolution of a portion as calcium aluminate
and its subsequent precipitation.   No precipitates were formed
in the strontia and baryta titrations, even although large excesses
of the reactants were added.

As Fig. 124 shows, aluminium chloride is almost completely
converted into aluminium hydroxide with alkalis.   Martin (*J. Soc.*

Chem. Ind., 1937, **59**, 179T) uses this fact to estimate aluminium in magnesium alloys by titrating a hydrochloric acid solution with alkali between the change-points of bromophenol blue (*p*H 3·7) and methyl red (*p*H 6). Under these conditions the magnesium remains in solution.

The electrophoretic mobility of colloidal aluminium hydroxide is a function of *p*H. From *p*H 3 to *p*H 6 there is a slight increase, from *p*H 6 to *p*H 9 the mobility as a positive colloid gradually diminishes to zero, and from *p*H 9 to *p*H 11 the mobility increases in the reverse direction (Hazel, *J. Physical Chem.*, 1938, **42**, 409).

Beryllium.

The other curve in Fig. 123, which represents the titration of beryllium sulphate, has two distinct sections in the acid zone. Precipitation was delayed until the beginning of the second section had been reached, when 1·04 equivalents of sodium hydroxide had been added. Thus the beryllium sulphate had to be rendered basic to the extent shown by the formula $BeSO_4,Be(OH)_2$, before a precipitate began to separate. Although the beryllium sulphate had become so basic, the solution remained perfectly clear and betrayed no sign of colloidality.

The fact that there was a marked inflexion in the hydrion curve just at the stage when half of the stoicheiometrical amount of sodium hydroxide had been added seems to indicate some fundamental difference between the first and second hydroxyl groups of beryllium hydroxide which gives rise to the formation of soluble basic salts in which the first beryllium valency is attached to the weaker hydroxide group. It must be stated, however, that concentrated solutions of beryllium sulphate can be rendered still more basic to the extent of 2 molecules of $Be(OH)_2$ to 1 molecule of $BeSO_4$. It is probable, whether the basic sulphate does or does not exist in solution as a definite chemical compound, that the solution is mainly colloidal in nature, in spite of the fact that it is clear and is not coagulated by electrolytes. The colloidal aggregates of beryllium hydroxide which probably exist in some type of combination with the sulphate groups appear to be capable of ionisation, although to a less extent than would have been the case had the sulphate radicals been united with beryllium simply. If these basic solutions happen to be examples of colloidal electrolytes, it would be expected that the solution of beryllium hydroxide in a beryllium sulphate solution, being brought about by the formation of aggregates of the beryllium hydroxide and the beryllium sulphate, would be accompanied either by a diminution in the number of osmotically active particles, partly present as

an ionisable colloid and partly in true solution, or, in the extreme and improbable case, by no change in number. Some support for this view is to be found in the observations of Parsons, Robinson, and Fuller (*J. Physical Chem.*, 1907, **11**, 651), who found that the effect of dissolving beryllium hydroxide in solutions of beryllium sulphate was to raise the freezing-point and to reduce the
* conductivity.

The beryllia on becoming completely precipitated retained sulphate and corresponded with $BeO,0.045SO_3$, for 1.9 equivalents of NaOH were necessary. The alkaline branch of the beryllium sulphate curve indicates *p*H values which would have been produced by an excess of alkali, and this was, in spite of the re-solution of the beryllium hydroxide which was taking place. The re-solution of the beryllium hydroxide was not complete when 90 c.c. of alkali had been added, which amount was a little in excess of that required to form sodium beryllate, Na_2BeO_2, neither did the titration curve give any indication that combination had taken place. The amount of alkali requisite for re-solution varies with the concentration of the alkali used (*vide* Britton, *Analyst*, 1921, **46**, 363).

Hydroxides of Zinc, Chromium, Bivalent Tin, and Zirconium.

The particulars of the titrations illustrated in Fig. 125 are given in Table 171. They were performed at 18° C. with the hydrogen electrode compared with the normal calomel electrode.

Zinc.

The zinc curve in Fig. 125 was obtained with the hydrogen electrode in the ordinary way. Various workers have questioned the behaviour of the hydrogen electrode in the presence of zinc ions, and Kolthoff and Kameda (*J. Amer. Chem. Soc.*, 1931, **53**, 832) claimed to have prepared hydrogen electrodes, covered with bright crystalline platinum, which gave accurate *p*H values during alkali titrations of zinc salts. These electrodes, however, appear to have been very easily incapacitated. With such electrodes they obtained *p*H values that were about one *p*H unit higher than those shown in Fig. 125. Incidentally, Prytz (*Z. anorg. Chem.*, 1931, **200**, 133) found that electrodes covered with platinum black give *p*H values in the case of alkali precipitation of zinc chloride solutions which are in good agreement with those found by Kolthoff and Kameda. Britton and Robinson (*Trans. Faraday Soc.*, 1932, **28**, 531) observed that bubbling hydrogen electrodes in zinc salt solutions tend to give what appears to be

reproducible data as long as the hydrogen is bubbled past the electrode, but that on stopping the flow of hydrogen and allowing the electrode to become immersed entirely in the solution there occurs a gradual drift in the potential, it ultimately indicating higher pH values, which are comparable with those shown by the glass electrode (see Fig. 125) and also with those recorded by Kolthoff and Kameda.
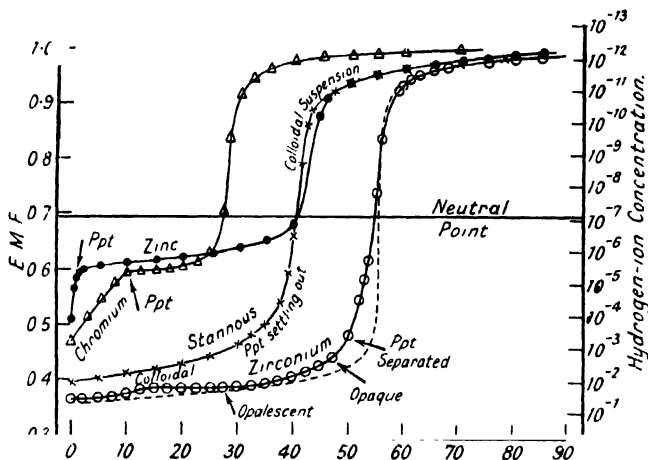
FIG. 125.—Precipitation of Hydroxides.

The zinc curves (Figs. 125 and 122) show that sodium hydroxide precipitates a basic sulphate from solutions of zinc sulphate.

Precipitation was complete when 1·53 equivalents of alkali had been added, which may have been due to the separation of a basic sulphate, $ZnSO_4,3ZnO,xH_2O$. As in other cases, the amount of alkali required was determined by the rate at which it was added, it appearing to be a rule that the more slowly the alkali is added, the less basic will be the precipitate ; this, once formed, is decomposed slowly by the further addition of alkali.

Complete re-solution of the zinc hydroxide did not take place in the course of the titration, although more than two molecules of sodium hydroxide were added in excess of that required to form zinc hydroxide. These measurements give no insight into the acidic nature of zinc hydroxide, for no inflexions occurred when alkali in amounts required to form the zincates having the respective formulæ $NaHZnO_2$ and Na_2ZnO_2 had been added. Calculation, however, shows that the concentration of hydroxyl ions in the alkaline solutions was slightly less than would have

TABLE 171

| Solution 100 c.c. | Normality of NaOH. | Precipitation Began. | | Precipitation Complete. |
		pH.	C.c. NaOH.	Equivs. NaOH.
0·025 M.-ZnSO₄ . . .	0·090	5·20*	0·6	1·53
0·005 M.-Cr₂(SO₄)₃, K₂SO₄				
(violet)	0·100	5·34	10·0	2·75
0·020 M.-SnCl₂ . . .	0·0932	—	—	1·86
		Opalescent at		
0·01 N-HCl	0·090	1·86	27·5	—
and		Precipitated at		
0·01 M.-ZrCl₄	0·090	2·79	47·5	3·75

been the case had no substances other than the alkali been present. For example, the *p*H of the solution containing the alkali required to form NaHZnO₂ was 12·06 as compared with the calculated value 12·25. It is probable that the diminution in hydroxyl-ion concentration was due both to some chemical action and to adsorption having taken place. This view is supported by the conductivity measurements of Chatterji and Dhar (Faraday Soc., " Symposium on Colloids," 1921, p. 123), who state that whereas the conductivity of sodium hydroxide was not appreciably changed by the addition of the majority of amphoteric hydroxides, the change when zinc hydroxide was added was pronounced. Similar observations were made by Carrara and Vespignani (*Gazzetta*, 1900, **30**, 35) with potassium hydroxide solutions of zinc hydroxide (see, however, Hildebrand and Bowers, *J. Amer. Chem. Soc.*, 1916, **38**, 785).

Chromium.

Chrome alum was used for the titration as it is the most suitable violet salt. The reader is referred to page 266 concerning differences between the violet and green forms. No precipitate was formed until one-third of the stoicheiometrical amount of sodium hydroxide had been added—the *p*H having previously rapidly increased until the precipitation *p*H was reached. The amount of alkali required to cause the beginning of precipitation seems to suggest that the basic salt retained in the solution had the formula Cr(OH)SO₄. It is probably a coincidence, for dissolved chromium sulphate can be rendered more basic and still remain in solution. The curve shows that the mother-liquor

* Should be *ca.* *p*H 7, see Table 168.

became alkaline when 2·75 equivalents of alkali had been added—an amount pointing to the final composition of the precipitate being $Cr_2O_3,0·25SO_3$. Williamson (*J. Physical Chem.*, 1923, **27**, 384) found, by adding varying amounts of sodium hydroxide to a decimolar solution of chrome alum, that when from 1 to 2·5 equivalents of alkali are added to one molecule of chrome alum the precipitates are almost constant in composition, $Cr_2O_3,0·7SO_3$, $3·6H_2O$, but when three equivalents are employed the precipitate is still more basic, as shown by the formula $Cr_2O_3,0·28SO_3,3·18H_2O$. This formula is similar to that indicated by the titration. Thus it appears that during the steady increase in pH shown when from 10 to 22 c.c. of alkali were being added, a basic sulphate of approximately constant composition was being formed, which after precipitation became more hydrolysed by the further addition of alkali.

The titration curve affords no evidence of the constitution of alkaline solutions of chromium hydroxide, although the amount of alkali which was added was in excess of that required to form Na_3CrO_3. The amount of alkali was insufficient to dissolve the chromium hydroxide. The potential differences obtained in the alkaline solutions pointed to hydroxyl-ion concentrations which were a little less than those obtained by calculation. The difference may probably be accounted for by adsorption by the chromium hydroxide or possibly by some little union having taken place. Fricke and Windhausen (*Z. anorg. Chem.*, 1924, **132**, 273) have also shown that there is a slight difference in hydroxyl-ion concentration observable between sodium hydroxide solutions and those of chromium hydroxide in sodium hydroxide of the same concentration when measured by the $Hg\,HgO$ electrode.

Stannous Tin.

The stannous chloride solution used in the titration shown in Fig. 125 was turbid and became more and more so until 30 c.c. of alkali had been added, when a heavy precipitate began to settle ; the precipitate passed back again into colloidal suspension as soon as the solution had become alkaline ($pH = 8·7$) and 41·0 c.c. of sodium hydroxide had been added. By calculating the amounts of hydrolysed hydrochloric acid from the titration pH data, it is possible to find the compositions of the basic stannous chloride aggregates at different stages in the titration. It will be found that they varied in composition from $SnCl_{1·33}(OH)_{0·67}$ to $SnCl_{0·55}(OH)_{1·15}$ during the addition of the 30 c.c. of alkali and yet remained in colloidal suspension. The molecular proportion of hydrochloric acid hydrolysed gradually became less as the

titration proceeded and it was not until the particles had become basic to the extent represented by the latter formula, and the concentration of the free hydrochloric acid with which they had existed in equilibrium had become relatively small, that the colloidal solution coagulated. The solution became neutral when 40 c.c. of alkali had been added, showing that chloride was still being retained by the stannous hydroxide, its composition having then become $SnCl_{0.11}(OH)_{1.86}$. The fact that peptisation of the precipitate took place immediately the mother-liquor became alkaline seems to be important, and it may be that the reaction of the alkali with the retained chloride in the precipitate was largely responsible. No inflexion was produced in the curve in the alkaline zone.

Zirconium.

The precipitation of zirconia from a solution in hydrochloric acid has been investigated (Fig. 125) and also the change in *p*H in the mother-liquor when the precipitated zirconium hydroxide was in the presence of an excess of sodium hydroxide. No inflexion was produced in the alkaline section, though one might have been expected if sodium zirconate had been formed. There appears to be absolutely no grounds for regarding zirconium hydroxide as amphoteric. Unlike the other hydroxides, that of zirconium is not dissolved by alkalis under any condition.

The titration curve gives some insight into the mechanism of precipitation. An aqueous solution, 0·04 Normal with respect to the chloride content, was hydrolysed immediately after preparation to the extent of 54 per cent. The dotted line in the diagram represents the neutralisation curve of hydrochloric acid solution having the same chloride concentration as that of the acid solution of zirconium chloride with the same alkali solution. The small but definite inflexion which occurred when 11·1 c.c. of alkali had been added marks the end of the neutralisation of the excess of acid over that required to form zirconium tetra-chloride. This is opposed to the generally accepted view that the chloride dissolves as " zirconyl chloride," $ZrOCl_2$, dissociating into " zirconyl " ions, $ZrO^{\cdot\cdot}$ and $2Cl'$, and free hydrochloric acid. The solution began to become opalescent when 27·5 c.c. of alkali had been added, and this was before the amount of alkali had been added which was necessary to form either $ZrOCl_2$(33·3 c.c.) or the basic salt from which the solution was prepared (36·2 c.c.). As solutions of both these substances happen to be perfectly clear, it follows that the premature opalescence obtained in the titration must have been due either to the electrolytes present or to the

hastened growth of the colloidal particles owing to the rate at which the alkali was added. It must have been due to the latter, for salts may be added to basic zirconium chloride solutions of similar composition without producing any perceptible effect. The zirconium chloride curve tends to approach the hydrochloric acid curve when approximately two equivalents of sodium hydroxide have been added (33·3 c.c.). At this stage the chloride radicals in combination with the zirconium were undergoing the maximum hydrolysis. The solution became increasingly colloidal in appearance as the alkali was added until it became opaque and coagulation suddenly took place (47·5 c.c.). Table 172 gives the fractions of zirconium chloride which had suffered hydrolysis and which had not entered into the reaction at the various stages in the titration, from which have been found the compositions of the unhydrolysed basic circonium chloride together with the molar proportions of the free acid which had been hydrolysed.

In these calculations it has been assumed that the hydrochloric acid was completely dissociated. The degree of hydrolysis of the zirconium chloride in the free acid solution was obtained by subtracting the hydrion concentration produced by the excess of acid from the total hydrion concentration calculated from the observed voltage.

TABLE 172

BASIC NATURE OF ZIRCONIUM SALT SOLUTIONS

C.c. of NaOH	E.M F. of $H_2	- $ N.Cal.	Atoms of Cl Neutralised.	Fraction of Unneutralised HCl Hydrolysed.	Comp of Basic Chloride to 1 Atom of Zr.		Mols. of HCl Hydrolysed.	Remarks.
				OH.	Cl.		
0	0·366	0	0·529	2·12	1·88	3·12	Free HCl
11·1	0·380	0	0·579	2·32	1·68	2·38	,,
22·2	0·386	1·0	0·670	3·01	0·99	2·01	Clear
27·8	0·390	1·5	0·714	3·28	0·72	1·78	Opalescent
33·3	0·393	2·0	0·828	3·66	0·34	1·66	,,
36·2	0·397	2·67	0·831	3·70	0·30	1·44	,,
38·9	0·406	2·5	0·685	3·53	0·47	1·03	,,
44·4	0·426	3·0	0·480	3·48	0·52	0·48	,,
47·5	0·444	3·28	0·333	3·52	0·48	0·24	Opaque
50·0	0·481	3·5	0·107	3·55	0·45	0·05	Coagulated
52·7	0·571	3·75	0·006	3·75	0·25	0·00	,,

It will be seen that the maximum hydrolysis occured when just over two equivalents of chloride of the zirconium chloride had been reacted upon, and that the rapid increase in hydrolysis during the

first portion of the titration was accompanied by a corresponding change in the composition of the basic zirconium chloride actually present in the solution (columns 5 and 6). Thereafter, the composition of the basic zirconium chloride remained nearly constant and corresponded roughly with the formula $Zr(OH)_{3.5}Cl_{0.5}$ until after coagulation occurred, when it was partially decomposed by the alkali. The first half of the titration, besides yielding a rapidly increasing basic chloride, was accompanied by a gradual decrease in the amount of free acid, which tended to render the basic zirconium chloride more and more insoluble and thus produced a gradual growth in the size of the basic chloride particles. At the beginning of the titration the particles probably approximated to molecular dimensions, but as the chloride became more and more basic these exceedingly small particles coalesced to form larger and larger aggregates until they became sufficiently big to render the solution opalescent, and this process still continued through the period when the solution had become visibly and increasingly colloidal right up to the point when coagulation occurred. The table shows that the free acid had some inhibiting effect on this growth in the size of the particles, for it was only after an appreciable proportion of the acid had been neutralised that the solution became opalescent. Very soon afterwards the basic chloride particles became uniform in composition, but coagulation did not occur until nearly all the free hydrochloric acid had been removed.

Colloidality of Zirconium Chloride Solutions.

These observations seem to suggest that the nature of basic zirconium salt solutions is essentially colloidal in spite of the fact that many of the solutions are perfectly clear. Müller (*Z. anorg. Chem.*, 1907, **52**, 316) arrived at the same conclusion from a study of the reactions of zirconium salt solutions. The observations, moreover, furnish an excellent example to show that the process of precipitation is one which involves the formation of a colloidal solution which subsequently coagulates. In the majority of precipitations the colloidal solution stage is so rapidly passed that it is not observed.

Adolf and Pauli (*Kolloid Z.*, 1921, **29**, 173) found that the hydrolysis of solutions of zirconium oxychloride, $ZrOCl_2$, of concentrations ranging from 0·0022 to 0·125 M., after 10 days' standing, varied irregularly between 35 and 50 per cent. A freshly prepared solution of zirconium chloride containing 1Zr : 1·737Cl was hydrolysed to the extent of 54 per cent., whereas, in the solution containing the basic chloride having the same com-

position in the course of the titration (Table 172) the hydrolysis
was considerably greater, *viz.*, 83·1 per cent. In the latter case,
the solution was opalescent and therefore contained larger par-
ticles than the corresponding clear solution. Thus the degree
of hydrolysis appears to be a function of the size of particle,
and consequently the smaller amount of hydrolysis in the clear
solutions of Adolf and Pauli must have been due to the presence
of particles which had been rendered small by the solvent-action
of the free acid. They prepared by dialysis zirconium oxide
hydrosols, which contained appreciable amounts of chloride ;
one contained 0·33 atom of chlorine and the other 0·26 atom
to each atom of zirconium. Both sols were hydrolysed to small
extents, *viz.*, 0·9 and 0·6 per cent. It is important to note that,
although the concentration of free acid was small, there was a
relatively large concentration of chloride ions, 41 and 37 per cent.
respectively of the total chlorine content. The ratio of Zr : Cl
in these hydrosols corresponds to points on the titration curve
lying between those representing 3·5 and 3·75 equivalents of
sodium hydroxide, *i.e.*, just after coagulation had taken place.
The amount of free acid was of the same order in both the
colloidal solutions and the mother-liquor in which the basic
zirconium precipitate was suspended. The large concentration
of chloride ions in the colloidal solutions shows that the basic
chloride particles do dissociate in some way.

Anomalous Behaviour of Zirconium Sulphate Solutions.

Solutions of zirconium sulphate behave towards some reagents
in a manner quite different from that of solutions of either the
chloride or the nitrate, so much so that Ruer (*Z. anorg. Chem.*,
1904, **42, 85**) and others have postulated that the sulphate must
exist in solution as a complex sulphuric acid in which the zir-
conium is present in a complex anion and thereby escapes pre-
cipitation. Thus oxalic acid and alkali metal oxalates fail to
precipitate it, and sulphites only precipitate it slowly and incom-
pletely. If potassium chloride be added to a zirconium sulphate
solution, either before or after the addition of sodium oxalate, the
solution becomes readily precipitable. Another point of differ-
ence is the behaviour towards sodium tartrate. Zirconium
chloride yields a precipitate with sodium tartrate, readily soluble
in excess, as compared with the precipitate which is obtained from
zirconium sulphate solution, which dissolves only on boiling or on
prolonged standing. The precipitate in the latter case is mainly
basic zirconium sulphate. Chauvenet (*Ann. Chim. Phys.*, 1920,
13, 82) titrated several zirconium salt solutions conductometrically,

and found that the titration curves, instead of being straight lines as in acid-alkali neutralisations, were slightly curved, such that the tangents drawn to the curves at each end intersected at points corresponding to approximately two equivalents of alkali. This he claimed to be evidence for the existence of the " zirconyl," ZrO¨, radical. The data given in the previous table show that during the addition of the first two equivalents of alkali the basic chloride undergoes hydrolysis and the remaining two equivalents cause little variation in its composition, $Zr(OH)_{3.5}Cl_{0.5}$, except at the end. These two processes, which took place in the precipitation from zirconium chloride solution, undoubtedly account for the change in the slope of Chauvenet's curve, which had therefore nothing to do with an alleged zirconyl radical. Chauvenet also titrated a solution of zirconium sulphate by the conductivity method and obtained the point of minimum conductivity when 3 equivalents of alkali had been added ; this he claimed to be due to the separation of a definite basic sulphate, $ZrOSO_4,ZrO_2$. He also claimed that an inflexion was produced when two equivalents of alkali had been added, which pointed to another definite basic salt, zirconyl sulphate, $ZrOSO_1$. In view of the peculiar properties shown by zirconium sulphate and of the contentions of Chauvenet, it was decided to subject the sulphate to titration with the hydrogen electrode.

The zirconium sulphate had the composition

$$ZrO_2,2\cdot10SO_3,2\cdot29H_2O,$$
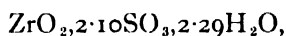
from which a $0\cdot01301$ M.-$Zr(SO_4)_2$ solution was prepared at room temperature ; therefore 100 c.c. of the solution contained uncombined sulphuric acid equivalent to 2·56 c.c. of N/10-alkali. The curve showing the titration with N/10 sodium hydroxide of 100 c.c. of this solution at 18° is given in Fig. 126. The first inflexion occurred when the added alkali was equivalent to 3 molecules to 1 molecule of zirconium sulphate. At this point precipitation was complete and the solid had the composition $ZrO_2,\frac{1}{2}SO_3$. The further addition of alkali (up to 50·4 c.c.) caused its partial decomposition and the mother-liquor became alkaline. The composition of the precipitate must then have been $ZrO_2,0\cdot16SO_3$, but the slope of the curve during the addition of the next few cubic centimetres of alkali shows that some alkali was still being withdrawn from the solution and utilised in decomposing the precipitate still more. The sulphate solution, unlike that of the chloride, began to yield a precipitate immediately the alkali was added. It is curious that by warming zirconium sulphate solution it may be made strongly basic by means of alkali

without the separation of a precipitate, the solution remaining quite clear. The dotted curve given in Fig. 126 is the titration curve of 100 c.c. of sulphuric acid containing 41·6 c.c. of N/10-sulphuric acid, equivalent in concentration to three-quarters of the combined acid in the zirconium sulphate solution together with the small amount of free sulphuric acid. The two curves are nearly coincident over the first half of the zirconium sulphate curve, but vary a little during the addition of the third equivalent. The curves show therefore that the zirconium sulphate solution contained a basic sulphate and free sulphuric acid in approximately
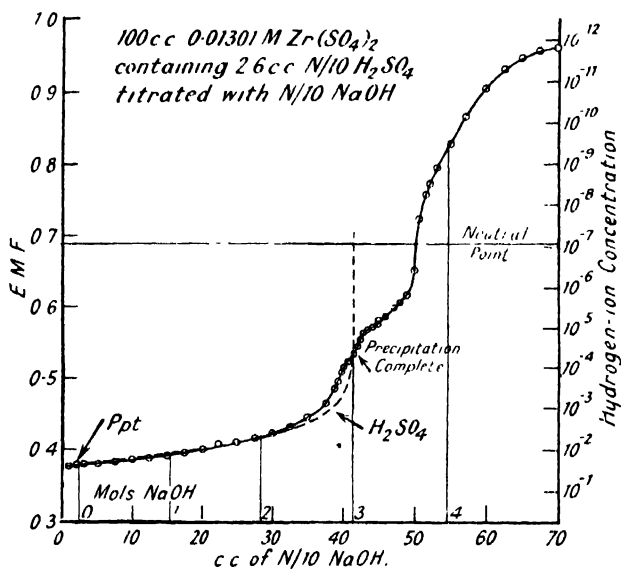
FIG. 126.—Precipitation of Basic Zirconium Sulphate.

the proportions 1 molecule of $ZrO_2,\frac{1}{2}SO_3$ to $1\frac{1}{2}$ molecules of H_2SO_4. The addition of alkali had the main effect of neutralising the free sulphuric acid, with the consequence that the basic sulphate with which it had existed in some kind of equilibrium was precipitated. The curves give no evidence of Chauvenet's so-called zirconyl sulphate, but do confirm his observation of the precipitation of a basic sulphate of approximately the composition $ZrO_2,\frac{1}{2}SO_3$. Further work, however, is necessary on the lines of the phase rule before its individuality can be established.

The view that these somewhat inert basic zirconium sulphate particles exist in solution in equilibrium with hydrolysed sulphuric acid gives an explanation of the abnormal behaviour of reagents towards zirconium sulphate solutions, especially that of sodium tartrate in precipitating the basic sulphate in such a state that it is not readily soluble in excess of the reagent.

The Cerite Group of Rare Earths and Yttrium.

A series of hydrogen electrode titration curves were obtained (Britton, *J. Chem. Soc.*, 1925, **127**, 2142) showing the changes in
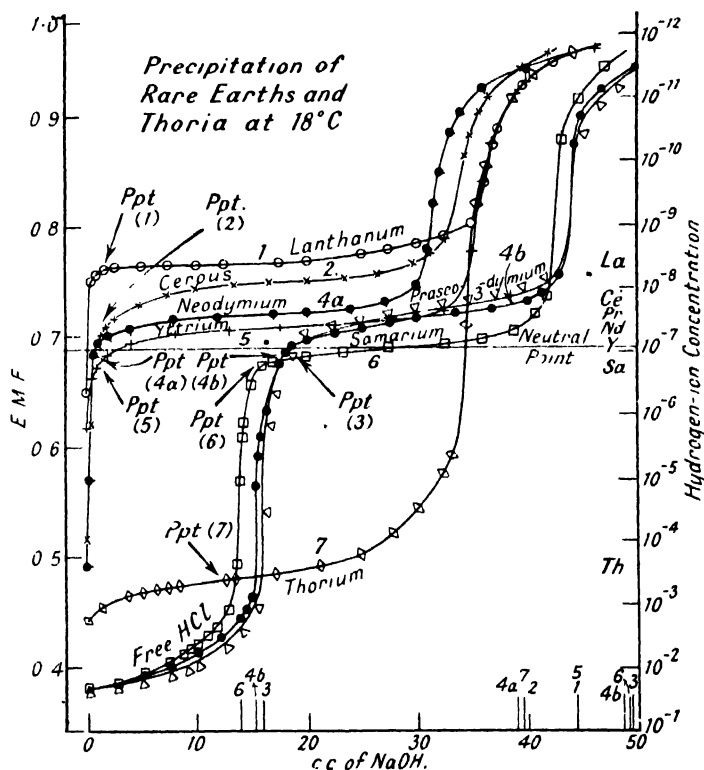
FIG. 127.—Precipitation of Thoria and Rare Earths.

hydrogen-ion concentration undergone during the precipitation of certain rare earths. Particulars of the solutions are given in Table 173, and the curves in Fig. 127.

D*

TABLE 173

RARE-EARTH SOLUTIONS TITRATED AT 18° C.

Titration and Curve No	Solution Titrated (100 c.c.)	Normality of NaOH.	Precipitation.		
			Began.		Ended.
			*p*H.	C.c. of NaOH	Equivs. NaOH.
1	0·0133 M.-La(NO₃)₃	0·090	8·35	1·0	2·60
2	0·0133 M.-CeCl₃	0·1018	7·41	1·8	2·61
3	(1) 0·0163 N-HCl	0·1018	—	—	—
	(2) 0 0114 M.-PrCl₃	—	7·05	18·2	2·45
4*a*	0·0133 M.-Nd(NO₃)₃	0·1018	7·00	0·8	2·38
4*b*	(1) 0·0154 N-HCl	0·1018	—	—	—
	(2) 0·0114 M.-NdCl₃	—	7·02	18·0	2·53
5	0·0133 M.-YCl₃	0·090	6·78	1·0	2·36
6	(1) 0·0140 N-HCl	0·1018	—	—	—
	(2) 0·0121 M.-SaCl₃	—	6·83	16·1	2·48

As thoria occurs with the rare earths in monazite sand, the titration curve (No. 7), of 100 c.c. of 0·01 M.-thorium chloride solution with 0·1016 N-sodium hydroxide, has been included in order that the precipitation *p*H of thoria might be compared with those of the rare earths. The great difference in the hydrogen-ion concentrations accounts for the ease with which thoria can be separated from the rare earths of the " cerite " group by those methods which depend on the change in *p*H. Knowing the respective hydrion concentrations it is possible to effect the separation of thorium hydroxide from the rare earths by carefully varying the *p*H of the solution by means of alkalis and suitable indicators. The hydrogen-ion concentrations may be varied : (*a*) by using reagents which impart hydrion concentrations to the solutions greater than those to be attained for the precipitation of the rare earths but less than that for thorium hydroxide, and (*b*) by fractional precipitation with bases which produce *p*H's which are greater than those produced by the bases to be separated. Methods employing the former device need no control, but those based on the latter principle must be controlled, either as regards the hydrion concentrations by means of indicators or electrometric measurements, or as regards the fractions themselves by determining their chemical equivalents ; which is the method usually adopted.

A method, based on the former principle, has recently been elaborated by Ismail and Harwood (*Analyst*, 1937, **62**, 185), in which hexamethylene-tetramine is used to separate thorium

hydroxide from the rare earths in monazite sand. In the presence of hydrogen ions, hexamine hydrolyses into formaldehyde and ammonia. The buffer action of the ammonium salts prevents the precipitation of the rare earths.

Basic thorium formate begins to precipitate at *p*H 4·45 and ends at approximately *p*H 5·3. (Willard and Gordon, *Anal. Chem.*, 1948, **20**, 165.)

The hydrogen-ion concentrations which were necessary for the precipitation of lanthanum and cerous hydroxides (curves 1 and 2) were appreciably less than those required for the other four earths. The differences in *p*H at which the earths praseodymia, neodymia, yttria, and samaria were precipitated, although very small in the case of the first three, were sufficient to indicate that these are precipitated in the order given, which is the order usually claimed. The closeness of the hydrion concentrations prevailing throughout the precipitations of the hydroxides of praseodymium, neodymium, and yttrium shows that a separation of these three earths by a hydrogen-ion concentration method is impracticable. The strongest base of the yttrium group is generally stated to be yttria, and according to these measurements, it appears to have a strength of the order of that of " didymia." Curves 4*a* and 4*b*, illustrating the respective titrations of the nitrate and chloride of neodymium, show, contrary to the observations of Hildebrand (*J. Amer. Chem. Soc.*, 1913, **35**, 847), that the hydrogen-ion concentration required for the precipitation of neodymium hydroxide is quite independent of the nature of the anion. The lower value obtained for the nitrate solution must have been due to the use of an electrode whose hydrogen was catalytically reducing the nitrate.

₊ The hydrogen-ion concentrations at which lanthanum and cerous hydroxides are precipitated are a little greater than that necessary for manganous hydroxide. It was therefore thought that the presence of ammonium chloride in sufficient quantity might prevent their precipitation with ammonium hydroxide (see p. 69). Calculation shows that, for each molecule of ammonia, 14 and 32 molecules, respectively, of ammonium chloride should be sufficient to prevent the precipitation of lanthanum hydroxide and cerous hydroxide. Actually, ammonium chloride has some inhibiting effect on the precipitation of the two hydroxides, and when the proportion of ammonium chloride to ammonium hydroxide is large, as indicated by the calculations, the precipitation can be entirely prevented.

Bowles and Partridge (*Ind. Eng. Chem., Anal. Edn.*, 1937, **9**, 124) obtained similar curves with the glass electrode during the

precipitation with alkali from approximately centimolar solutions of various rare-earth salts. In addition to their data, listed in Table 174 they found that precipitation occurred at pH 2·75 from ceric ammonium sulphate and pH 2·65 from ceric sulphate solutions. Very often, these pH values are situated on the steep initial inflexions of the curves, but the precipitations take place mainly at the somewhat higher pH values, indicated by the subsequent gradual rise in pH. It follows that oxidation of cerous salts to the ceric state permits of the separation of ceria with alkali from the other rare earths as is the case with thoria.

Precipitation of Mercuric, Cadmium, Lead, Silver, Cupric, Uranic, and Ferric Hydroxides, investigated with the Oxygen Electrode.

On account of the inapplicability of the hydrogen electrode to solutions of salts of the above bases, resort was made to the oxygen electrode (*J. Chem. Soc.*, 1925, **127**, 2148), and in order to get an approximate idea of the variations which occurred in the concentrations of hydrogen ions, the salt solutions were acidified to known concentrations whose pH values could be calculated. They were titrated with alkali, and from the excesses added the final pH values could also be found. The voltages of the oxygen electrode-normal calomel electrode combination found for each titration could then be resolved into pH values merely by simple proportion (*cf.* p. 93, Vol. I). With the exception of the silver nitrate titration, for which a saturated potassium nitrate solution had to be used as the junction liquid for obvious reasons, these proportional pH scales might be considered as indicating values with an accuracy of about a 0·5 pH unit.

It will be seen from Table 175 that under the conditions of gradual precipitation the hydroxides are, in general, not obtained, but precipitates containing basic salts. Thus, copper sulphate solutions when subjected to careful treatment with alkalis, in quantities less than three-quarters of the amounts requisite for the complete decomposition of the salt, yield precipitates of $4CuO,SO_3,4H_2O$, which has been proved by phase rule methods to be a definite basic salt (Britton, *J. Chem. Soc.*, 1926). It may be that the precipitates obtained in titrations 1, 2, and 3 were basic salts of similar composition, *viz.*,

$$3HgO,HgCl_2,xH_2O$$
$$3Cd(OH)_2,CdSO_4,xH_2O$$
and $$3Pb(OH)_2,Pb(NO_3)_2,xH_2O.$$
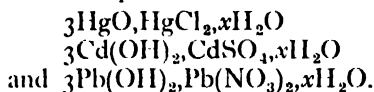
A basic precipitate was not obtained from a silver nitrate solution,

TABLE 174

PRECIPITATION OF HYDROXIDES OF THE RARE EARTH METALS

	*p*H at incidence of pptn.				*p*H on addn. of 0·4 equiv. NaOH/R⋯ (M.K.).		
	NO_3'	Cl'	Ac'	SO_4''	NO_3'	Ac'	SO_4''
La	8·35 B. 8·71 O. 7·82 M.K.	8·03 B.P.	7·93 M.K.	7·61 B.P. 7·41 M.K.	8·23	8·13	7·78
Cl	8·1 O. 7·60 M.K.	7·41 B.	7·77 M.K.	7·07 B.P. 7·35 M.K.	7·76	7·99	7·56
Pr	7·35 M.K.	7·05 B.	7·66 M.K.	6·98 B.P. 7·17 M.K.	7·67	7·96	7·50
Nd	7·00 B. 7·31 M.K.	7·02 B. 7·40 B.P.	7·59 M.K.	6·73 B.P. 6·95 M.K.	7·40	7·65	7·23
Sa	6·92 M.K.	6·83 B.	7·40 M.K.	6·70 M.K.	7·08	7·48	6·93
Eu	6·82 M.K.		7·18 M.K.	6·68 M.K.	6·90	7·37	6·82
Gd	6·83 M.K.		7·10 M.K.	6·75 M.K.	6·94	7·31	6·95
Y	7·39 O. 6·95 M.K.	6·78 B.	6·83 M.K.	6·83 M.K.	6·90	7·15	6·90
Er	6·76 M.K.	.	6·59 M.K.	6·50 M.K.	6·84	6·93	6·58
Tm	6·40 M.K.		6·53 M.K.	6·21 M.K.	6·70	6·77	6·38
Yb	6·30 M.K.		6·50 M.K.	6·16 B.P. 6·18 M.K.	6·65	6·73	6·32
Lu	6·30 M.K.		6·46 M.K.	6·18 M.K.	6·63	6·73	6·32
Sc			6·1 S.B.M.				

B.P. = Bowles and Partridge, *Ind. Eng. Chem., Anal. Edn.*, 1937, **9**, 124.
B. = Author.
O. = Oka, *J. Chem. Soc., Japan*, 1938, **59**, 971.
M.K. = Moeller and Kremers, *J. Physical Chem.*, 1944, **48**, 395 ; *Chemical Reviews*, 1945, **37**, 97.
S.B.M. = Štěrba-Bohm and Melichar, *Coll. Czech. Chem. Com.*, 1935, **7**, 131.

TABLE 175

Titration and Curve No.	100 c.c. of Solution contained :		NaOH Normality	Precipitation *p*H (approx).	Equivs. NaOH for Complete Precipitation.
	Free Acid.	Salt.			
1	0·0212 N-HCl	0·02 M.-HgCl₂	0·1018	7·4	1·5
2	0·0199 N-H₂SO₄	0·02 M.-CdSO₄	0·1018	6·7	1·5
3	0·0202 N-HNO₃	0·02 M.-Pb(NO₃)₂	0·1005	6·0	1·5
4	0·0202 N-HNO₃	0·02 M.-AgNO₃	0·1018	—	2·0
5	0·0199 N-H₂SO₄	0·02 M.-CuSO₄	0·1018	5·4	1·47
6	0·0149 N-HNO₃	0·00833 M.-U(NO₃)₆	0·1005	4·2	5·93
7	0·0202 N-HCl	0·0133 M.-FeCl₃	0·1005	opalesc. 2·3 coag. 6·6	2·35 1·85

and the uranic and ferric hydroxide precipitates contained only relatively small amounts of undecomposed salt.   Fig. 128 shows in titration No. 6 that precipitation was complete when 64 c.c. of alkali had been added as compared with the 64·7 c.c. which were required for the complete formation of uranic hydroxide.   Hence the pre-
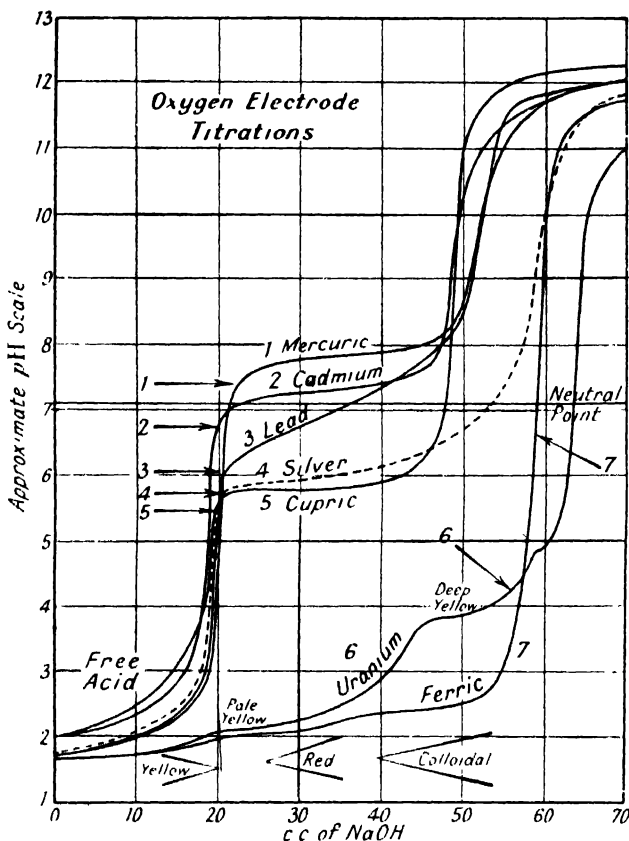
FIG. 128.—Oxygen Electrode Titrations involving Precipitations.

cipitate was uranic hydroxide containing a very small quantity of undecomposed nitrate.   Text-books state that alkalis precipitate " diuranates " and not uranium hydroxide ;   e.g., with sodium hydroxide, the precipitate is stated to be $Na_2U_2O_7$ (compare Roscoe and Schorlemmer's *Treatise*, Vol. II., p. 1154, revised 1923). , Jollibois and Bosnet (*Compt. rend.*, 1922, **174**, 1625) found that the precipitates produced by the action of sodium hydroxide

on uranyl nitrate solutions contained no nitrate ; the small quantities of sodium hydroxide present, varying from 1·2 to 8 per cent., they considered to be adsorbed.

The approximate pH values at which the various precipitates began to form from the dilute solutions used are given in Table 175. Although the oxygen electrode is of considerable service in electrometric titrations, the pH values, which its potentials may be considered to show, are far from satisfactory. The correct pH ranges of precipitation of these bases should be measured by more accurate methods, e.g., with the glass electrode, or when applicable, with the quinhydrone electrode.

The pH ranges, indicated by the oxygen electrode, in which precipitation occurs from mercuric chloride, lead nitrate and copper sulphate solutions, compare satisfactorily with those given by the glass electrode as shown in Fig. 122. On the other hand, the glass electrode curves corresponding with the precipitation of silver oxide from silver nitrate solution reveal that the oxygen electrode pH values were about two pH units too low. Britton and Young (*J. Chem. Soc.*, 1932, 2467), who studied the precipitation of uranic hydroxide using the quinhydrone electrode, found that precipitation occurs at pH values which are about 0·5 pH higher than shown in Fig. 127. The errors introduced during the precipitation of silver oxide and uranic hydroxide are evidently to be attributed to the oxidising tendencies of the silver and uranium precipitates.

Glass Electrode Titrations involving the Precipitation of Hydroxides.

Fig. 122 gives a number of pH precipitation curves of solutions of the various metallic salts, shown on the curves, with sodium hydroxide. Except for the 0·005 M.-$CuSO_4$ and 0·02 M.-$CuSO_4$ curves, which were obtained by Westmoreland-White, and Britton and Meek respectively with the quinhydrone electrode, the curves were obtained with the glass electrode by Britton and Robinson (*Trans. Faraday Soc.*, 1932, **28**, 532), Dorling (Ph.D. Thesis, London, 1936, p. 87—$Pb(NO_3)_2$ curve) and Hughes (*J. Chem. Soc.*, 1928, 491—1M.-$CuSO_4$ curve).

Precipitation almost invariably began as soon as the pH had risen to a value which marks the main section of the curve corresponding to the precipitation process. The $AgNO_3$ and $CuSO_4$ curves in the upper part of Fig. 122, and the zinc curves, lower part, illustrate the effect which the concentration of the metallic salt has on the pH at which precipitation occurs. The zinc curves also reveal the small effect which an anion may occasionally

have on the pH of precipitation. From the amount of sodium hydroxide, shown by the position of the final inflexion, required for complete precipitation, it appears that a less basic zinc salt, *viz.*, $ZnSO_4,3Zn(OH)_2$, separates from the sulphate solutions than from chloride solutions. It is probable that a much less basic zinc chloride initially precipitates which becomes attacked as the alkali is added.

The $Pb(NO_3)_2$ curve shows that precipitation is complete with three-quarters of the stoicheiometric amount of alkali, indicating the composition of the precipitate to be $Pb(NO_3)_2,3Pb(OH)_2$. The wide precipitation range, extending from pH 6 to pH 8, suggests that a less basic precipitate is first formed which subsequently undergoes hydrolysis.

Fig. 122 shows that, despite the high pH at which magnesium hydroxide precipitates, the glass electrode yields a curve exactly comparable with that given by the hydrogen electrode (Fig. 123).

The mercurous nitrate curve refers to the titration of a solution of 0·0168 N-HNO_3 + 0·05705 M.-$HgNO_3$ with alkali. The neutralisation of the excess acid, during which a slight precipitate appeared, is marked by a small inflexion. Thereafter the precipitate was black, but soon became green, when a drift in pH to lower values occurred. Precipitation occurs in the vicinity of pH 3. Bennett (*J. Physical Chem.*, 1934, **38**, 573), however, found that precipitation begins slightly above pH 4 and continues to pH 4·9.

Moeller (*J. Physical Chem.*, 1941, **45**, 1235 ; *J. Amer. Chem. Soc.*, 1941, **63**, 2625) has shown with the glass electrode that indium hydroxide precipitates at pH 3·41 from 0·05 M. indium sulphate, but not until 0·85 equivalent of NaOH has been added.

Glass Electrode Investigation of the Amphoteric Nature of Auric Oxide.

Preliminary glass-electrode titrations of $HAuCl_4$ solutions indicated that the pH values set up on the addition of alkali were dependent on the length of time allowed before making observations. This was due, not to sluggishness of the glass electrode, but to the slowness of the attack of the alkali on the $HAuCl_4$. Curves A and B (Fig. 129) are the titration curves of 50 c.c. of 0·004 M.-$HAuCl_4$ with 0·0392 N-NaOH added in 2-c.c. portions, the potentials being measured, respectively, as rapidly as possible (within 1 minute) and 5 minutes after the addition. Neither of these two curves was reproducible. Curve C, however, which

refers to a series of solutions of constant volume that had stood until no further reaction occurred, as indicated by *p*H changes, is reproducible. The time required was about 2 days. Curves 1, 2 and 3 give further evidence of the time required for the reaction of 4–4·5 molecules of alkali, since they represent respectively the reaction after ½, 1, and 3 hours.

Owing to the dilution of the solutions used, no auric oxide
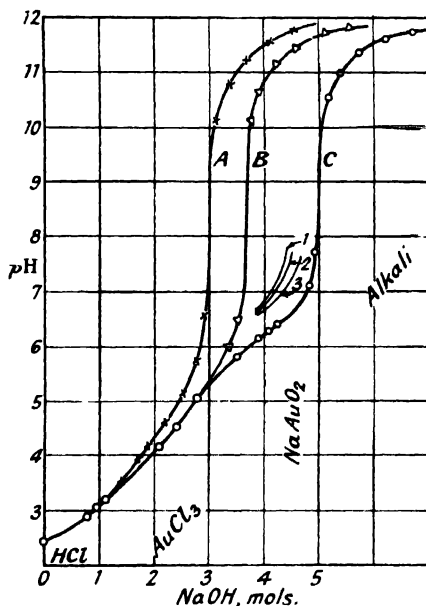
Fig. 129.—Glass Electrode Titrations of HAuCl, with NaOH.
(Britton and Dodd, *J. Chem. Soc.*, 1932, 2464)

was precipitated. The *p*H of the HAuCl$_4$ solution showed that 6·45 per cent. of the AuCl$_3$ present was hydrolysed, and when the equivalent of HCl was neutralised the hydrolysis increased to 23·3 per cent. Hence the first stage of the titration may be represented as the neutralisation of the hydrolysed hydrochloric acid, thus

$$HAuCl_4 + xH_2O \rightarrow (1 + x)HCl + AuCl_{3-x}(OH)_x.$$
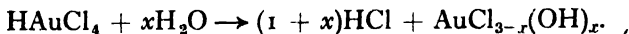
The lack of simple ionisation and the probable heterogeneous nature of the basic gold chloride would explain why the attack of alkali is a time reaction as shown by the direct electrometric titration curves A and B. According to Hittorf and Salkovsky (*Z. physikal.*

Chem., 1899, **28**, 546), auric chloride exists in solution in the form

$$H_2O + AuCl_3 \rightleftharpoons H_2AuOCl_3 \rightleftharpoons 2H^{\bullet} + AuOCl_3''.$$

They showed that the gold existed in the complex anion. It is likely that in these titrations the initial effect of the alkali was to react with the basic gold chloride to form a stable negatively charged complex, thus :—

$$NaOH + AuCl_{3-x}(OH)_x \longrightarrow Na^{\bullet} + AuCl_{3-x}(OH')_{x+1},$$

which, as the result of the subsequent slow reaction, broke down to give sodium aurate, $NaAuO_2$ (Curve C), and sodium chloride. The complex nature of the auric chloride solutions is also apparent from its reactions with silver nitrate and silver carbonate : Jacobsen (*Compt. rend.*, 1908, **146**, 1213) states that the precipitate obtained with the former is $4AgCl,Au(OH)_3$, whilst Hittorf and Salkovsky (*loc. cit.*) state that with the latter it is Ag_2AuOCl_3.

Glass Electrode Titrations of Mercuric Salt Solutions with Alkali.

In general, none of the anions, NO_3', Cl' and SO_4'', has any appreciable effect on the pH values at which metallic bases undergo precipitation, owing to the fact that the corresponding salts of any particular metal ionise to similar extents in solutions of the comparable concentrations. With bivalent mercury conductivity measurements reveal that the salts of strong oxyacids, nitric, sulphuric, perchloric, are considerably dissociated, whilst the reverse is true of the chloride, bromide, cyanide, nitrite and acetate. Whereas the salts of the strong oxyacids are appreciably hydrolysed, so much so that it is necessary to have an excess of the free acid to prevent the precipitation of basic salts, mercuric chloride, bromide, etc., are not only almost un-ionised but they are also almost un-hydrolysed in aqueous solution. As shown on page 88, the solubility product principle is roughly obeyed when a basic salt, instead of the hydroxide, is precipitated by the addition of alkali. Hence, it would be expected that the very great variations in mercuric-ion concentration of the various mercuric salt solutions would be reflected in the pH at which alkali causes precipitation.

Fig. 130 represents glass electrode titrations of 100 c.c. of each of the mercuric salt solutions specified below, the last column giving the legend of the corresponding curve.

The effect is illustrated in Fig. 130, in which the buffered ranges, which begin soon after the first few drops of alkali have been added, represent the variations in pH during the precipitation process. Owing to the almost complete lack of mercuric ions,

sodium hydroxide causes no precipitation from mercuric cyanide solutions, and as the uppermost curve in Fig. 130 shows, the added alkali merely passes into solution as such.
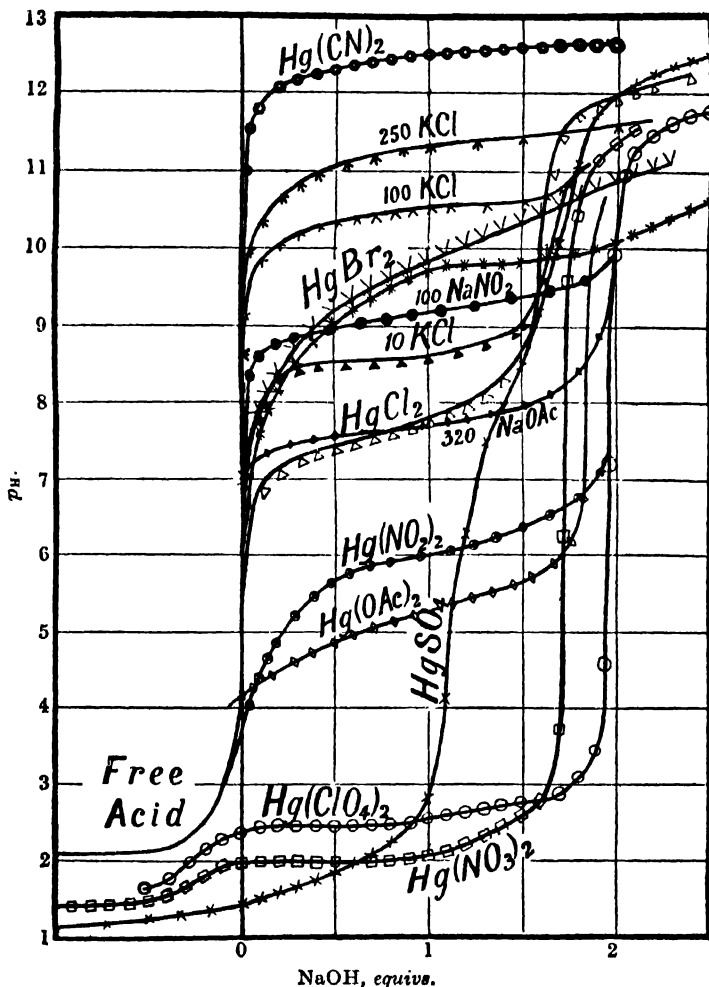
FIG. 130.—Precipitation from Mercuric Salt Solutions with NaOH.
(Britton and Wilson, *J. Chem. Soc.*, 1932, 2550.)

Basic precipitates were obtained in each of the other cases, as may be seen from the final inflexions occurring before two equivalents of NaOH were added.

When combined with strong acids mercuric oxide behaves as

a normal weak base, and although mercuric nitrate, sulphate and perchlorate are appreciably hydrolysed, there is evidence that they ionise fairly extensively : Morse (Z. physikal. Chem., 1902, **41**, 709) found that a dilute solution of mercuric nitrate containing an equimolar amount of nitric acid was about 40 per cent. ionised. The ionic product, $[Hg^{..}][OH']^2$, set up during the precipitation of basic mercuric nitrate, can thus be roughly ascertained from the pH value and the concentration of mercuric nitrate left in solution at any particular stage, the assumption being made that the basic nitrate indicated by the inflexion of the curve was precipitated from the beginning : the values thus found range from 0·3 to 0·7 × 10^{-26}, which agree sufficiently well with the solubility product of mercuric oxide, viz., 1 × 10^{-26} (p.99, Vol. I).

TABLE 176

Hg Salt and Concn. M.		Added Acid and Concn. M.	Added Salt and Concn M	NaOH. N.	Curve.
HgCl₂,	0·025	—	—	0·1019	HgCl₂
,,	0·010	—	KCl, 2·478	0·1000	250KCl
,,	0·010	—	,, 0·994	0·1000	100KCl
,,	0·010	—	,, 0·0994	0 1000	10KCl
HgBr₂,	0·00305	—	—	0·0100	HgBr₂ (upper)
,,	0·00526*	—	—	0·0200	HgBr₂ (lower)
Hg(CN)₂,	0·025	—	—	0·0992	Hg(CN)₂
HgSO₄,	0·0251	H₂SO₄, 0 0969	—	0·200	HgSO₄
Hg(NO₃)₂,	0 02446	HNO₃, 0·02296	— -	0 0994	Hg(NO₃)₂
Hg(ClO₄)₂,	0·02576	HClO₄, 0·01337	—	0·0994	Hg(ClO₄)₂
Hg(NO₃)₂,	0·01023	HNO₃, 0·00196	NaNO₂, 0·02046	0·0992	Hg(NO₂)₂
,,	0 01023	,, 0·00196	,, 1·087	0 0992	100NaNO₂
Hg(OAc)₂,	0·00932	HOAc, 0·00040	—	0·0992	Hg(OAc)₂
,,	0·00466	—	NaOAc, 1·5	0·0992	320 NaOA

* Higher concentrations of HgBr₂ could not be used owing to the sparing solubility of the salt.

Precipitation from mercuric chloride solutions can be explained in terms of the equilibrium, $HgCl_2 \rightleftharpoons Hg^{..} + 2Cl'$, which Luther (Z. physikal. Chem., 1901, 36, 385) and Morse (loc. cit.) have found may be represented by $K = [Hg^{..}][Cl']^2/[HgCl_2]$. For K, Luther gave 1·5 × 10^{-14} and 0·18 × 10^{-14}, whilst Morse reported 1·0 × 10^{-14}. Taking the last value, and assuming (a) that only the chloride-ion concentration originating from the sodium chloride formed during the precipitation with alkali was of sufficient magnitude to have any effect and (b) that the concentration of undissociated mercuric chloride was equal to that of the unattacked

mercuric chloride, it was possible to calculate the mercuric-ion concentration at any stage of the precipitation. Hence, in conjunction with the *p*H value, the following solubility products were calculated.

Using Morse's value, $K = 2 \times 10^{-18}$, governing the ionisation of mercuric bromide, similar calculations can be made.

The titration curves also explain why an excess of a strong acid in a solution of either mercuric nitrate, sulphate or perchlorate can be titrated to methyl orange if sufficient alkali chloride or bromide has first been added to form the respective mercuric halide, thus :—

$$Hg(NO_3)_2 + 2NaCl \longrightarrow 2NaNO_3 + HgCl_2.$$
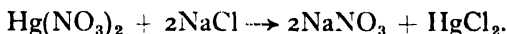
The curves, marked 10, 100 and 250 KCl, reveal that mercuric

TABLE 177

TITRATION OF 100 C.C. OF 0·025 M.-HgCl$_2$ WITH
0·1019 N-NaOH

NaOH equivs..		0·2	0·4	0·6	0·8	1·0	1·2	1·4
*p*OH	. . .	7·14	6·93	6·78	6·64	6·47	6·29	5·96
[Hg''] × 10^{13} .	.	58·7	13·2	5·1	2·4	1·3	0·6	0·2
[Hg''][OH']^2 × 10^{26} .		3·1	1·8	1·4	1·2	1·4	1·5	2·6

chloride in the presence of such molecular proportions of potassium chloride in yielding smaller concentrations of mercuric ions do not begin to precipitate until higher *p*H values are established.

In presence of much alkali chloride mercuric salts are converted into complex salts in which the mercury exists in the anion, HgCl$_4$''. Abegg and Sherrill (*Z. Elektrochem.*, 1903, **9**, 549) found that ionisation of this anion, HgCl$_4$'' $\leftrightharpoons$ Hg'' + 4Cl', was governed by [Hg''][Cl']^4· [HgCl$_4$''] $=$ K, for which *p*K - 15·95. Pick (*Z. anorg. Chem.*, 1906, **51**, 20) obtained 16·30 for *p*K. By assuming also that the ionic product [Hg''][OH']^2 during the precipitation from solutions of mercuric chloride in the presence of large amounts of potassium chloride had the value 1×10^{-26}, it was possible to calculate [Hg''], and, if all the mercuric chloride is converted into HgCl$_4$'' ions, [HgCl$_4$''] and [Cl'] could be found and *p*K evaluated. The degrees of ionisation, α, in the 10KCl and 100KCl titrations were taken as 0·848 and 0·772 respectively. The typical values of *p*K, given in Table 178, are of the same order as those previously obtained.

The Reaction of Ammonia with Mercuric Chloride, etc.

The two lower curves in Fig. 131 represent the progressive precipitation from mercuric chloride solution with sodium

hydroxide and ammonia respectively. With ammonia the precipitate first formed is very pale yellow and bulky, but immediately after the inflexion the precipitate changes into a white, heavy, granular form. Two precipitation processes are involved : (i) the formation of a basic chloride $HgO,xHgCl_2$, (ii) the formation of a basic precipitate containing mercuric chloride with which two molecules of NH_3 are co-ordinated, thus $HgO, y(HgCl_2,2NH_3)$. The composition of the resulting precipitate may thus be represented a HgO, b $HgCl_2$, c NH_3. If the precipitate has stood in contact with a solution containing free ammonia,

TABLE 178

TITRATION OF 100 C.C. OF 0·01 $M.-HgCl_2(+$ 0·09944 N-KCl) WITH 0·111 N-NaOH

NaOH, equivs.	$pH.$	$pH_g''.$	$pHgCl_4''.$	$pCl'.$	$pK.$
0·7	8·54	14·6	2·27	1·12	16·8
1·0	8·67	14·9	2·45	1·10	16·8
1·3	8·83	15·2	2·73	1·08	16·8

TITRATION OF 100 C.C. OF 0·01 $M.-HgCl_2(+$ 0·9944 N-KCl) WITH 0·1 N-NaOH

0·7	10·47	18·5	2·22	0·15	16·9
1·0	10·56	18·7	2·34	0·16	17·0
1·3	10·61	18·8	2·51	0·17	16·9

then c becomes equal to $2b$. Immediately after precipitation, c is less than $2b$. In the reverse titration, upper curve, in which mercuric chloride was run into an ammonia solution, the formation of a basic chloride without co-ordinated ammonia was prevented and the precipitate was white, characteristic of ammoniated mercuric compounds. As the curve shows, the precipitation process came to an end when 0·5 molecule of $HgCl_2$ was added to 1 molecule of NH_4OH.

The reaction can thus be represented by the

$$2xNH_4OH + 2(1 - x)NH_3 + HgCl_2 \rightarrow$$
$$xH_2O + 2xNH_4Cl + \underbrace{xHgO,(1 - x)(HgCl_2,2NH_3)}_{\text{Precipitate}}$$
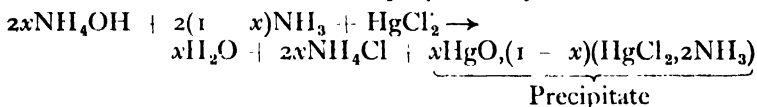
from which it would follow that if 2 molecules of NH_4OH are not required to form 1 molecule of HgO, 2 molecules of NH_3 must be taken up unattacked by each molecule of $HgCl_2$ that

passes into the precipitate.   If precipitation takes place in this manner throughout the titration, then the amount of ammonia left unattacked is known at any stage, and as the value of $[NH_4Cl]/[NH_4OH]$ can be calculated from the *p*H value, the $[NH_4Cl]$ in solution, and consequently the NH_3 and Cl present
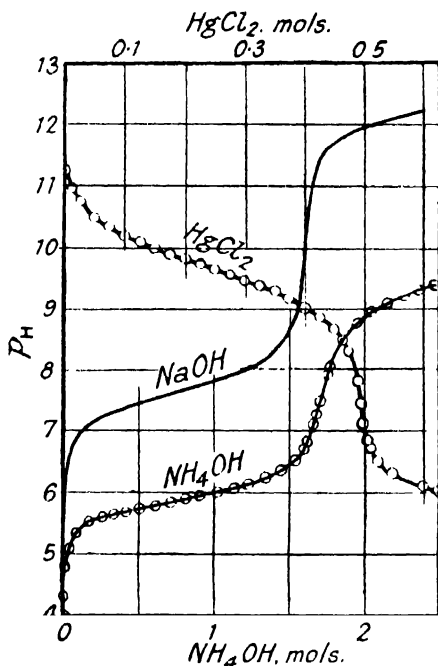
FIG. 131.—Glass Electrode Precipitation Curves of Mercuric Chloride with Ammonium Hydroxide.

Upper curve : 100 c.c. 0·1 N-NH₄OH titrated with 0·1 M.-HgCl₂.
Lower curve : 100 c.c. 0·025 M.-HgCl₂ titrated with 0·1027 N-NH₄OH.
Middle curve : 100 c.c. 0·025 M.-HgCl₂ titrated with 0·1 N-NaOH.

(Britton and Wilson, *J. Chem. Soc.*, 1933, 601.)

in the precipitate, can be ascertained.   Table 179 gives the details of such computations based on the titration of 100 c.c. of 0·100 N-NH₄OH with 0·1 M.-HgCl₂ at 16°.

The precipitate indicated by the last line is

$$HgCl_2,2NH_3,2·6HgO.$$

By using more concentrated solutions less basic ammoniated mercuric chlorides are obtained.   For instance, the method given in the British Pharmacopœia (1914, p. 177) for the preparation

of " infusible white precipitate " involves the interaction of stoicheiometric amounts by the gradual addition of 0·18 M.-HgCl$_2$ to approximately N-NH$_4$OH. The precipitate corresponds very closely with HgO,HgCl$_2$,2NH$_3$, or, after the removal of H$_2$O, with the more usual, but improbable, formula HgNH$_2$Cl. The entrance into the precipitate of the co-ordinated ammonia confers on it less solubility than that of mercuric oxide, or of allied basic salts. This can be seen from Fig. 131, which shows that ammonia causes precipitation at pH values about 2 pH units lower than sodium hydroxide. Calculation shows that the ionic product, [Hg··][OH′]^2, during precipitation with ammonia is 10^{-29} as compared with 10^{-26}, the solubility product of mercuric oxide ; *i.e.*, ammonia causes precipitation when the ionic product is *one-thousandth part* of the solubility product. This explains why ammonia is able to cause precipitation from alkaline mercuri-iodide

TABLE 179

HgCl$_2$ Added,		pH	pOH	[NH$_4$Cl]/[NH$_4$OH].	NH$_4$Cl in Soln , Mols.	Combined with Hg.	
C.c.	Mols per 1NH$_3$.					Cl.	NH$_3$.
10·0	0·10	10·18	4·02	0·21	1·65	0·35	0·35
20·0	0·20	9·81	4·30	0·49	1·47	0·53	0·53
30·0	0·30	9·47	4·73	1·07	1·43	0·57	0·57
40·0	0·40	9·05	5·16	2·88	1·44	0·56	0·56

solutions, *viz.*, Nessler's reagent (*cf.* Britton and Wilson, *J. Chem. Soc.*, 1933, 1045). The precipitate obtained is essentially 3HgO,HgI$_2$2NH$_3$, instead of the formula NHg$_2$I ordinarily assigned.

As the magnitudes of [Hg··] and [OH′] are the determining factors in precipitations with ammonia, then it would appear that the magnitude of the dissociation constant of ammonium hydroxide will determine whether the requisite pH can be established at which the ionic product 10^{-29} can be exceeded. Now, although mercuric chloride forms analogues of fusible white precipitate with many organic bases, *e.g.*, ethylamine, aniline, pyridine, quinoline, and urea, yet the last four are too weak to give basic chloride precipitates (containing the organic base) when added directly to mercuric chloride, evidently because they cannot maintain pH values high enough for basic precipitation to take place. By adding concentrated alkali and alkali carbonate solutions to solutions of mixtures of mercuric chloride and urea, however, Pesci (*Z. anorg. Chem.*, 1897, **15**, 232) prepared the urea analogues

of infusible white precipitate and of the so-called chloride of Millon's base.

The precipitation of a less basic chloride, $HgO,HgCl_2,2NH_3$ (*i.e.*, infusible white precipitate, $NgNH_2Cl$), by the use of a more concentrated solution of ammonia may appear to be at variance with the views expressed above. Two influences, however, come into play : (1) the diminished ionisation of the ammonium hydroxide, due to the increased concentration, and consequent production of a relatively smaller [OH'] and greater [NH₃] ; (2) the solubility of mercuric oxide in saline solutions (*cf.* p. 100) including those of ammonium salts. If the concentration of ammonium chloride formed during the reactions at higher concentrations exceeds that with which the particular final solid phase is in equilibrium (*cf.* Strömholm, *Z. anorg. Chem.*, 1908, **57**, 80), it will dissolve mercuric oxide from the complex basic precipitate,

$$HgO + 2NH_4Cl \rightarrow HgCl_2,2NH_3,$$
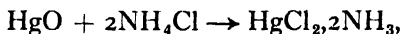
and the product is ultimately reprecipitated.

Many of the methods of preparing fusible white precipitate, $HgCl_2,2NH_3$, make use of precipitation with concentrated solutions of ammonia from mercuric chloride solutions in which much ammonium chloride has been dissolved. The latter salt not only tends to dissolve the former but also forms a complex, $(NH_4)_2HgCl_4$ with it, so reducing the mercuric-ion concentration and raising the *p*H at which precipitation occurs on addition of ammonia, and thus tending to prevent the precipitation of mercuric oxide in the product. Although fusible white precipitate and mercuric oxide are but sparingly soluble in water at room temperature, both are more soluble in concentrated solutions of ammonia, especially if ammonium chloride is present.

Britton and Wilson have also shown that similar conditions apply to the precipitation with ammonia from mercuric bromide, nitrate, sulphate and perchlorate solutions.

Arrangement of Metals in the Order of the Hydrogen-Ion Concentrations required for the Precipitation of their Hydroxides.

It was stated on page 57 that no principle has yet been found which leads to a satisfactory arrangement of the metals in the order of the basic strengths of their hydroxides. The titrations described in the foregoing pages show that for each hydroxide there is a narrow range of hydrogen-ion concentration within which its precipitation normally takes place from dilute solutions. Table 180 gives the metals in the order of the hydrogen-ion

concentrations at which their respective hydroxides or basic salts are precipitated from dilute solutions. Although it is not certain that this order is that of the actual basic strengths of the hydroxides, it can be stated, as will be shown later, that it is these hydrogen-ion concentration relationships which underlie many of the reactions of the various metallic salt solutions.

If the order of the precipitation of the hydroxides is actually that of their basic strengths, the basic strengths of the rare earths are a little lower than those of manganous hydroxide and magnesium hydroxide. Lanthanum hydroxide is always stated to be the strongest base of the rare earths, and the " cerite " group of hydroxides, excepting ceric hydroxide, to be the group of the

TABLE 180

HYDROXIDE PRECIPITATION pH's FROM DILUTE SOLUTIONS

Hydroxide or Basic Salt.

Magnesium	.	.	.	10·5	Beryllium	.	.	.	5·7
Silver	.	.	.	7·5 -8·0	Ferrous	.	.	.	5·5
Manganous	.	.	.	8·5-8·8	Cupric	.	.	.	5·3
Lanthanum	.	.	.	8·4	Chromium	.	.		5·3
Cerous	.	.	.	7·4	Uranic	.	.	.	4·2
Mercuric (chloride)	.		7·3	Aluminium	.	.	.	4·1
Praseodymium	.	.	7·1	Mercurous	.	.	.	3
Neodymium	.	.	7·0	Thorium	.	.	.	3·5
Zinc	.	.	.	7·0	Indium	.	.	.	3·4
Samarium	.	.	.	6 8	Ceric	.	.	.	2·7
Cobalt	.	.	.	6·8	Mercuric (nitrate)	.		2
Yttrium	.	.	.	6·8	Stannous	.	.	.	2
Cadmium	.	.	.	6·7	Zirconium	.	.	.	2
Nickel	.	.	.	6·7	Ferric	.	.	.	2
Lead	.	.	.	6·0					

strongest bases. Apart from lanthanum hydroxide and perhaps cerous hydroxide, the other earths appear to be quite moderate in strength and are comparable with cobalt and nickel hydroxides. This is contrary to the view generally held. Little, (in Friend's " Text-Book of Inorganic Chemistry," 1917, Vol. IV., p. 257) states that " from general chemical and thermochemical considerations it may be concluded that they [the rare earths] are stronger than magnesia, but weaker than the alkaline earths." The chemical considerations are epitomised thus : " The strongly ignited oxides are readily soluble in mineral acids, several of them combine directly with water and absorb carbon dioxide from the air, and all of them liberate ammonia from cold solutions of ammonium salts. Normal salts of numerous weak acids, *e.g.*, chromic, carbonic, are readily prepared." The fact that a base forms well-defined salts with weak acids probably offers no clue to its strength, if those salts happen to be almost insoluble. This

is the case with the carbonates and chromates of the rare earths (*vide* Britton, *J. Chem. Soc.*, 1924, **125**, 1875). Thus thorium hydroxide is an exceedingly weak base, but under certain conditions it forms an extremely well-defined chromate; under other conditions it behaves like other weak bases and gives precipitates which are indefinite and basic (*vide* Britton, *ibid.*, 1923, **123**, 1429). The power to form well-defined salts with weak acids seems to be a property inherent in an element in conferring a small solubility on a salt and probably has nothing whatsoever to do with its power to form a strong base. There is no marked difference between the stability of acetates of the metals whose hydroxides are precipitated at comparable hydrogen-ion concentrations, *e.g.*, zinc, cobalt, nickel and cadmium.

An arrangement now widely adopted is that based by Abegg and Bodländer (*Z. anorg. Chem.*, 1899, **20**, 453) on their theory of electroaffinity, which states that the Normal Electrode Potential provides an approximate measure of the basic strength of the metal. Comparison with the present arrangement brings out the following important differences. According to the position of aluminium in the table, aluminium hydroxide is an extremely weak base, weaker than chromium hydroxide, yet aluminium occurs higher than chromium in the Electropotential Series. There is no doubt that both aluminium and chromium hydroxides are much weaker bases than manganous hydroxide, and this is also indicated by the present scheme, but according to the electropotential series they both are placed above manganese. Heyrovský (*Proc. Roy. Soc.*, 1923, *A*, **102**, 628) has pointed out that the thallous potential is small, which necessitates placing thallium relatively close to hydrogen in the electropotential series, in spite of the fact that 'thallous hydroxide is a strong base and is not precipitated by alkalis. If it be assumed that the electrolytic potentials of metals under identical conditions are a measure of their electroaffinities, *i.e.*, the free energies by which the elements take up electric charges, it cannot be concluded, as was admitted by Abegg and Bodländer, that these potentials are in any way parallel to the electroaffinities, for nothing is known of the relative atomic solubilities of the various metals in water. Unless it is known that the number of atoms of the different metals which pass into solution is the same, no guarantee can be obtained that an arrangement accruing therefrom is in any way true. Heyrovský attempted to amend the above method by introducing such factors as the mass of the cation, and obtained an order which he considered to be satisfactory, although the system indicates that lead hydroxide is a stronger base than magnesium hydroxide, whereas Table 180

suggests the contrary. It is probable that the pH series of metallic hydroxides is the most satisfactory arrangement which has yet been advanced, and from the hydroxide precipitation pH, it is an easy matter to state whether or no a precipitate will be produced when solutions of their respective salts are reacted upon by certain reagents. The salt solutions of the bases are found to be hydrolysed to a greater extent, as the hydroxide pH becomes lower and lower, so much so, that those of the bases at the bottom of the pH series are very considerably hydrolysed. It is with solutions of such salts that colloidal effects become apparent, and delay the appearance of a precipitate until a proportionately large amount of precipitant has been added. For such bases, it is not easy to assign with any certainty the pH at which precipitation actually does take place.

Controlled Separations.

These hydroxide precipitation pH's may be used to facilitate many separation processes, and, indeed, the separations may even be controlled by using a suitable indicator, either colorimetric or electrometric, of the hydrogen-ion concentration. Thus Ralston (*Trans. Amer. Electrochem. Soc.*, 1923, **43**, 87) found the oxygen electrode to be of considerable use for this purpose in the hydrolytic purification of electrolytes, such as the freeing of copper sulphate from traces of ferric hydroxide. Many analytical separations have been so worked out that the procedures themselves automatically control the hydrogen-ion concentration in such a way that the pH for one hydroxide is exceeded, whereas that of another is not. This is especially the case in the use of ammonium chloride, for, as shown on page 73, the buffering effect produced by 0·08 molecule to 1 of ammonium hydroxide is all that is necessary to prevent the attainment of the magnesium hydroxide pH, and 4·5 molecules to prevent the precipitation of manganous hydroxide. Again, in either the basic acetate or basic succinate methods of separating iron from manganese, the buffering action of the partly-neutralised acid maintains a hydrogen-ion concentration of about pH 5, which compels the ferric hydroxide to be precipitated at pH 2, but is sufficient to retain the manganous hydroxide in solution, as it is not precipitated until nearly pH 9 is reached.

Willard and Tang (*Ind. Eng. Chem., Anal. Edn.*, 1937, **9**, 357) have shown that a complete separation of aluminium from large amounts of Ca, Ba, Mg, Mn, Co, Ni, Zn, Fe'', Cd and Cu may be effected by boiling the acid solution, the solution having been acidified with succinic acid, with urea. Gradual hydrolysis liberates ammonia which causes the precipitation of aluminium

as a dense basic succinate and automatically sets up a *p*H between
4·2 and 4·6.

Lundell and Knowles (*J. Amer. Chem. Soc.*, 1923, **45**, 676) have
shown that the separation may equally well be performed by frac-
tional precipitation with ammonia in the presence of ammonium
chloride, the precipitation of the ferric hydroxide being ensured by
rendering the solution just alkaline to methyl red, *i.e.*, about
*p*H 6·3. Darbishire (*Industrial Chemist*, 1927, 172) has pointed
out that the standard method of separating manganese from both
iron and aluminium in, for example, the analysis of manganiferous
silicates by precipitating the latter two as basic acetates from very
dilute neutral solutions by boiling with sodium acetate involves a
difficult precipitation, a re-precipitation, tedious filtrations, and is
such as can scarcely be regarded as accurate except when carried out
with considerable care and skill. When the estimations are to be
carried out volumetrically, he advocates the use of finely powdered
zinc oxide as separating agent, which precipitates the aluminium
and ferric hydroxides and leaves the manganese in solution. The
principle underlying this procedure is apparent from Table 180.
Zinc hydroxide sets up a *p*H of 7 and thus falls between that of
manganous hydroxide, *p*H 8·8, and aluminium hydroxide, *p*H 4·14,
and ferric hydroxide, *p*H 2. It is essential that all iron in the
solution shall be in the oxidised condition, for ferrous hydroxide
begins to precipitate at *p*H 5·5. Lassieur (*Ann. chim. anal.*, 1926
[ii], **8**, 97 ; *Compt. rend.*, 1926, **182**, 384) has recently shown that
magnesia can be separated from alumina by means of ammonia
if sufficient only be employed to raise the *p*H to 7, as may be indi-
cated by the appearance of the blue tint of bromothymol-blue ;
beyond *p*H 7 some magnesium hydroxide was carried down. The
table also explains why mercuric oxide can be used as a separating
agent for various bases in chloride solutions. Thus E. F. Smith
and Heyl (*Z. anorg. Chem.*, 1894, **7**, 87) showed that mercuric
oxide caused the complete precipitation in the cold of ferric,
aluminium, and chromium hydroxides, the partial precipitation
of zinc, cobalt, nickel, uranium, beryllium, cerous, and lanthanum
hydroxides, but failed to precipitate manganous hydroxide from
chloride solutions. The table shows that the hydrogen-ion con-
centration peculiar to mercuric oxide, provided that it is in chloride
solution, is greater than that required to precipitate manganous
hydroxide, is approximately equal to that required for lanthana,
is somewhat less than that required by those hydroxides which
were partly precipitated, and is considerably less than that of the
three bases· which were completely precipitated.

Fig. 132 gives the types of curves which are obtained when

the changes in hydrogen ion undergone during separations are followed electrometricaily using suitable electrodes. Thus the curve A corresponds to the pH changes when N/10-NaOH is added to a solution, about ·100 c.c. in volume, and containing sulphuric acid equivalent to 20 c.c. of alkali, ferric sulphate to 40 c.c., and manganous sulphate to 40 c.c., or in case of dotted curve copper sulphate equivalent to 40 c.c. in place of the manganous
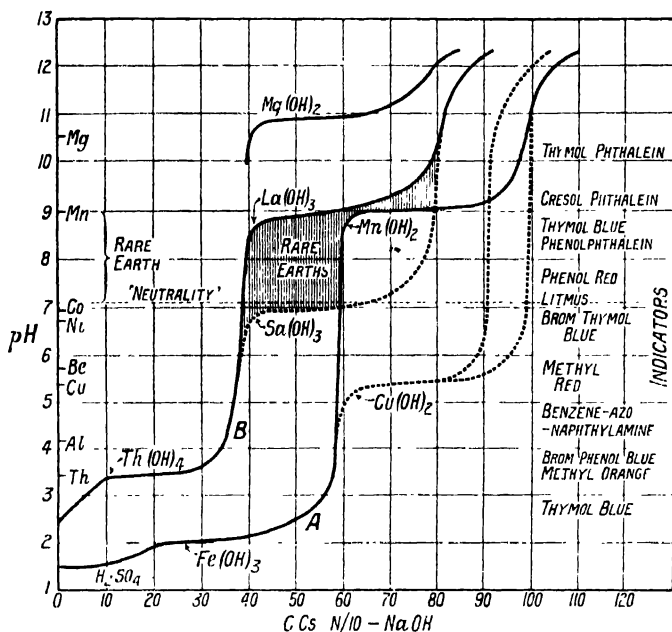
FIG. 132. —Curves showing how Hydroxides may be separated by taking advantage of variations in hydrogen-ion concentrations on addition of alkali.

salt. It should be mentioned that when the weaker bases, such as ferric hydroxide, stannous hydroxide and zirconia, are dissolved in hydrochloric acid, there is a pronounced tendency for the precipitate to remain in colloidal solution, which does not coagulate until somewhere in the region of pH 7 has been attained, but this does not obtain with sulphuric acid solutions. It will be seen from the diagram that the colour-change of methyl red corresponds with that pH when all the iron has been precipitated. The iron-copper separation, however, involves pH's which are probably too close together to be regulated by any other method than the electrometric method, with the oxygen electrode as used by Ralston or with the glass electrode. Curve B corresponds to

mixtures of thorium salt, equivalent to 40 c.c. of alkali, and a rare earth salt, say, lanthanum sulphate or samarium sulphate, equivalent to 40 c.c. The precipitation *p*H's of other rare earths which have been investigated fall within the shaded area lying between the lanthanum and samarium curves. Hence the thoria may be separated by neutralising the solution to methyl red. Reagents which have been used to effect this separation and which automatically control the *p*H in order that it may fall between the precipitation *p*H's are zinc oxide, *p*H 7·0 ; copper oxide, *p*H 5·4 ; certain very weak organic bases, *e.g.*, quinoline, *p*-toluidine (Jefferson, *J. Amer. Chem. Soc.*, 1902, **24**, 540 ; Allen, *ibid.*, 1903, **25**, 421 ; Hartwell, *ibid.*, p. 1128) ; sodium thiosulphate, and buffered solutions of hydrazoic acid (*i.e.*, acidified sodium azide). The precipitation *p*H's of praseodymia, 7·05, and neodymia, 7·00, are nearly identical, and therefore explain why these earths could not be fractionally precipitated with ammonia. The difference between the *p*H for lanthana and that for cerous cerium is too small to permit of a separation based on this principle, but when cerium is oxidised to the ceric state, the *p*H of precipitation, as ceric hydroxide, then becomes about 3, and enables separation to be effectively carried out. This process could be facilitated considerably by the use of indicators or the glass or oxygen electrodes, the hydrogen electrode being useless in presence of ceric salts.

Another separation which has been the subject of much work is that of aluminium from beryllium, these two metals occurring together in beryl, the chief source of the exceptional metal beryllium (*vide* Britton, *Analyst*, 1921, **46**, 359, 437 ; 1922, **47**, 50). Table 170 shows that the precipitation *p*H of aluminium hydroxide is 4·14, and of beryllium hydroxide 5·69, and their proximity therefore accounts for the great difficulty in separating the two metals by a method based on this principle. The presence of tannin in a solution of beryllium and aluminium salts greatly facilitates the precipitation of the respective hydroxides together with tannin when their hydroxide precipitation *p*H's have been set up in the solution. The precipitates which are voluminous are, no doubt, the result of the mutual coagulation of oppositely charged sols, the hydroxide being positive and the tannin negative. Moreover, there is a smaller variation in *p*H during the course of the precipitation of a tannin complex than is usually the case during the precipitation of the hydroxide alone and this often facilitates a separation. Thus Sears and Gung (*Ind. Eng. Chem.*, *Anal. Edn.*, 1944, **16**, 598 ; see also Nichols and Schempf, *ibid.*, 1939, **11**, 278) found that by adding ammonium hydroxide to a solution of beryllium and aluminium salts and tannin, containing

a suitable buffer system, until pH 4·6 was reached the aluminium was quantitatively precipitated.   A pH of 4·6 was located by the purple red of a mixed or " screened " indicator, prepared by adding 1 part of 0·1 per cent. solution of methyl red to 6 parts of bromocresol green (0·1 per cent. solution).

CHAPTER XXV

PRECIPITATION OF BASIC CHROMATES, BORATES, CARBONATES, AND SILICATES

THE author has correlated the formation of basic precipitates involving weak acids with that of the hydroxides, or, more generally, with that of the basic precipitates obtained by reaction with alkalis. The solutions investigated were of the same or comparable concentrations (*J. Chem. Soc.*, 1926, 125 ; 1927, 425), and the reactions were followed with the hydrogen electrode against the normal calomel half-element.

I. Basic Chromates.

Table 181 gives the particulars of the solutions and the *p*H's at which precipitation of basic chromates began, and these are com-

TABLE 181

PRECIPITATION OF BASIC CHROMATES

Solution (100 c.c.).	Precipitation of Basic Chromate began · *p*H.	Precipitation of Hydroxide began . *p*H	Precipitation.
0·01 M.-ThCl$_4$	3·45	3 51	Complete
0·00667 M -Al$_2$(SO$_4$)$_3$.	4·18	4·14	,,
0·01 M.-Cr$_2$(SO$_4$)$_3$,K$_2$SO$_4$.	5·20	5 34	,,
0·02 M.-BeSO$_4$ . . .	5·72	5·69	,,
0·025 M.-ZnSO$_4$ . . .	5·49	7·0	,,
0 0132 M.-Nd(NO$_3$)$_3$ . .	6·48	7·00	Partial
0·0133 M.-SaCl$_3$ . . .	6·55	6·83	,,
0·0133 M.-YCl$_3$ . .	6·74	6·78	,,
0·0247 M.-CoCl$_2$	7·01	6·81	,,
0·0200 M.-NiCl$_2$	6·78	6·66	Opalescence

pared with the respective hydroxide *p*H values. The titration curves are given in Fig. 133, the arrows indicating the points at which precipitates first appeared. M/10-potassium chromate was used in each titration except that of thorium chloride, in which case the concentration was M/20.

Mechanism of the Precipitation of Basic Chromates.—Table 181 shows that in the majority of the titrations a precipitate did not

form until the hydrogen-ion concentration of the solution had become that at which the hydroxide separates.   In one or two cases the precipitate first formed was the hydroxide uncontaminated with any chromate.   This was particularly the case with aluminium, the initial precipitate being aluminium hydroxide together with some unattacked sulphate.   The chief factor controlling the concentration of hydrogen ions is the reaction between the acid, produced from the metallic salt by hydrolysis, and the
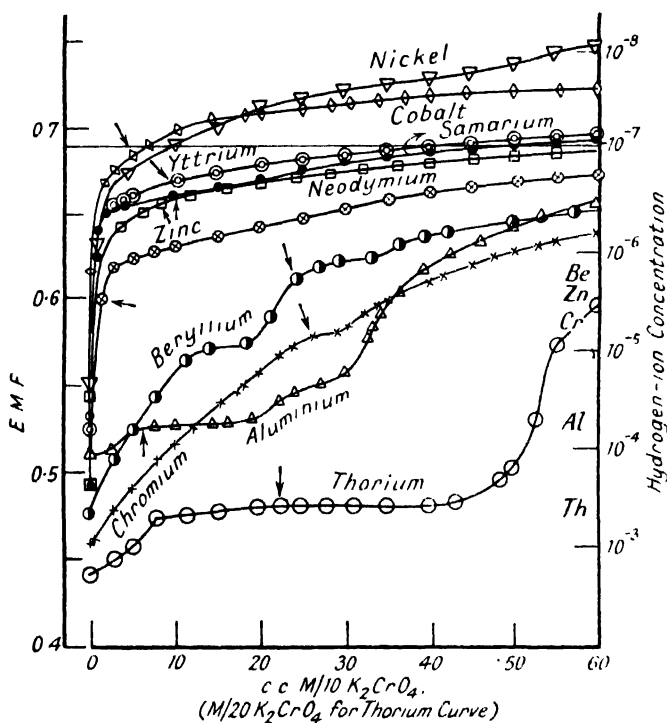
FIG. 133.—Precipitation of Basic Chromates.

potassium chromate, thereby liberating hydrochromate ions. The dissociation of these ions is exceedingly small and is rendered still smaller by the increasing concentration of chromate ions from the added potassium chromate.   The range of hydrogen-ion concentrations which can be produced in equilibria involving chromate and hydrochromate ions is 10^{-5} to 10^{-8}, as may be seen from the second section of the chromic acid titration curve (p. 212, Vol. 1). For a considerable range of equilibria the hydrogen-ion concentra-

tion remains approximately 10^{-6}. The reason, why potassium chromate precipitates basic chromates from salt solutions, lies in the inability of the hydrochromate ions to react with the metallic bases and thus to maintain them in solution, except in the few instances in which insoluble normal chromates are formed. For example, consider the reactions between freshly precipitated aluminium hydroxide and the hydrochromate ions present in potassium dichromate solutions of different concentrations. It can be shown that the pH of M/10- and M/100-KHCrO$_4$ is 3·68 and 4·18 respectively, by assuming the salts to be completely dissociated into K$^{\cdot}$ and HCrO$_4{}'$, and the latter ions to be dissociated further into an equal number of hydrogen ions and chromate ions. As aluminium hydroxide is precipitated at pH 4·14, it follows that at the moment of formation of the precipitate the hydroxyl-ion concentration of the solution is $K_w/10^{-4·14} = 10^{-10}$. In order that the aluminium hydroxide may react with the hydrochromate ions and consequently dissolve, the hydrochromate ions must be capable of providing sufficient hydrogen ions to form water with the hydroxyl ions in the solution, i.e., the product [H$^{\cdot}$][OH$'$] must be greater than K_w. If M/100-potassium hydrochromate solution be added to freshly precipitated aluminium hydroxide, it will set up a hydrion concentration of $10^{-4·18}$, which, being less than the precipitation hydrion concentration, will be incapable of causing solution, or, in other words, [H$^{\cdot}$][OH$'$] will become equal to $10^{-14·18}$, a value just less than K_w, $10^{-14·14}$. With M/10-KHCrO$_4$, pH = 3·68, the hydrogen-ion concentration will be less than that necessary for the precipitation of aluminium hydroxide and consequently there will be a tendency for the aluminium hydroxide to dissolve, the product being $10^{-13·68}$ which just exceeds the ionic product of water at 18°. If thorium hydroxide, however, be used, no reaction can take place, for its precipitation pH being 3·5, the product of the hydroxyl-ion concentration and the hydrion concentration arising from either M/10- or M/100-solution of the potassium acid chromate will be less than K_w.

The hydroxides occupying higher positions on the pH scale become increasingly reactive with the hydrochromate ions, though very little reaction takes place with those hydroxides which are precipitated from acid solutions. This is due to the fact that as soon as some hydrochromate ions have been converted into chromate ions, the hydrogen-ion concentration becomes considerably reduced and so prevents further reaction. As the hydrion concentration thereby produced is about 10^{-6}, its effect will be most marked with those hydroxides whose precipitation pH's are

above 7. The reaction between those hydroxides, which are precipitated at pH 7 and above, and the hydrochromate radical becomes more pronounced and consequently potassium chromate causes either partial or no precipitation. Thus it is clear why potassium chromate fails to precipitate magnesium salt solutions. Magnesium hydroxide is precipitated at pH 10·5 and is therefore able to react with the ions produced in the second stage of the ionisation of chromic acid to an extent sufficient to prevent the attainment of the pH of precipitation. Manganous hydroxide, too, is sufficiently strong (pH 8·4) to enter appreciably into combination with the hydrochromate radical. No precipitate is formed when potassium chromate is added to a manganous salt solution, but after some time the solution deepens in colour and eventually a brownish-black precipitate appears. This, however, is due to oxidation of the relatively large amount of manganous hydroxide present in the alkaline solution by the chromate and to some extent by the air (Gröger, *Z. anorg. Chem.*, 1905, 44, 453).

The foregoing reactions may also be considered from the point of view of the alkalinity of the potassium chromate solutions. By assuming complete ionisation of the various salts involved in the hydrolysis of potassium chromate solutions, it can be shown that $[\text{H}^{\bullet}] = \sqrt{\text{K}_2\text{K}_w/\text{C}_{\text{K}_2\text{CrO}_4}}$, K_2 of chromic acid at 18°, being $4\cdot4 \times 10^{-7}$. Therefore the pH of M/10-potassium chromate is 9·75 and of the M/100-solution, 9·25. Hence the addition of potassium chromate solutions in either of these concentrations to magnesium salt solutions cannot cause precipitation, as the reactants are incapable of attaining an alkalinity corresponding to the pH of precipitation of magnesium hydroxide. On the other hand, it appears at first sight that if a dilute manganous salt solution contained (say) M/100-potassium chromate, the hydrogen-ion concentration, *viz.*, $10^{-9\cdot25}$, which the latter would impart, would be less than that at which manganous hydroxide is precipitated (pH 8·4). The reaction between manganous chloride (say) and potassium chromate involves a ready reaction between manganous hydroxide and the hydrions from the first stage of ionisation of chromic acid to form some $\text{Mn}(\text{HCrO}_4)_2$ and also the more difficult reaction with the hydrions from the second stage. The result is that instead of the reaction being one of simple double decomposition, thus $\text{K}_2\text{CrO}_4 + \text{MnCl}_2 = \text{MnCrO}_4 + 2\text{KCl}$, the formation of a precipitate depends on how far the following equilibrium reaction is disturbed :

$$\text{Mn}(\text{HCrO}_4)_2 + \text{Mn}(\text{OH})_2 \rightleftharpoons 2\text{MnCrO}_4 + 2\text{H}_2\text{O},$$
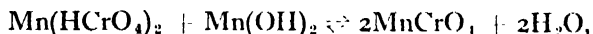
which is governed, the oxidation effects peculiar to manganous

and cobaltous hydroxides being excluded, by the two reactions:

$$(a)\ HCrO_4' + OH' \rightleftharpoons CrO_4'' + H_2O,$$
and $$(b)\ Mn^{\bullet\bullet} + 2OH' \rightleftharpoons Mn(OH)_2.$$
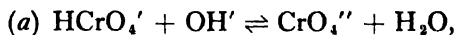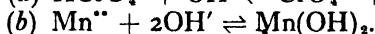
Equilibrium (a) is dependent on K_2 and K_u, and equilibrium (b) on $[Mn^{\bullet\bullet}][OH']^2$ or, more directly, the pH of precipitation. Thus it follows that when M/10-potassium chromate is added to a manganous salt solution of the concentration used in these titrations, the pH of the solution barely attains the precipitation pH of manganous hydroxide and no precipitate is at first produced. More concentrated solutions of potassium chromate, however, effect partial but almost immediate precipitation of basic manganous chromate.

The behaviour of potassium chromate towards nickel and cobalt salt solutions is of interest. As shown in Table 165, nickel hydroxide is precipitated at pH 6·66 and cobalt hydroxide at pH 6·81. Yet when M/10-potassium chromate is added to solutions of cobalt and nickel salts partial precipitation occurs in the former case and merely an opalescence is produced in the latter. The nickel and cobalt curves show that potassium chromate produces hydrion concentrations less than those at which the respective hydroxides are precipitated by alkali. The partial precipitation of cobalt is probably due to the tendency of cobalt hydroxide to oxidise. Gentle warming of the nickel solution is sufficient to cause precipitation.

The curves showing the course of precipitation of the basic chromates of neodymium and samarium have been included, for unlike the other metals, except thorium, they form well-defined, sparingly soluble salts and thus the precipitation of one or the other is determined by (a) the hydrogen-ion concentration, and (b) the solubility of the normal chromate.

These hydrogen-ion relationships of the various hydroxides explain why solutions of potassium dichromate, in spite of their pH's being greater than the precipitation pH's of certain hydroxides, fail to cause the precipitation of basic chromates, except from zirconium salt solutions; and even in this case it is far from complete. Unless concentrated solutions are used, in which case the normal thorium chromate may be precipitated, the addition of potassium dichromate to thorium salt solutions fails to give a precipitate, although the pH of the dichromate solution itself is greater (3·68–4·18 for solutions ranging from 0·1 M. to 0·01 M.) than the hydroxide precipitation pH 3·5. Potassium dichromate behaves, towards a weak base like thorium hydroxide, as a salt of a strong monobasic acid containing no reactive hydrogen atom,

and on addition to a thorium salt solution merely sets up an equilibrium, $ThCl_4 + 4KHCrO_4 \rightleftharpoons Th(HCrO_4)_4 + 4KCl$, in which the thorium salt is largely hydrolysed, and thereby maintains a hydrion concentration in the solution which is much greater than that required for the precipitation of the hydroxide. An excess of potassium dichromate will have a buffering effect on the hydrolysed chromic acid, but, as the first section of the chromic acid titration curve shows, the excess would have to be considerable before the hydrogen-ion concentration could be reduced to pH 3·5.

Detailed Study of the Precipitation Reactions.

Thorium.—Partial precipitation results when either M/100-thorium nitrate or chloride solutions are treated with M/20-potassium chromate in the stoicheiometrical amounts, and the precipitates contain thoria and chromic anhydride in the molecular ratio of 1 : 1·38. Fig. 133 shows that 22·7 cc.. of M/20-potassium chromate caused the attainment of the hydroxide precipitation pH, at which point basic thorium chromate began to be precipitated. The next 30 c.c. caused little change in pH, but soon afterwards a rapid diminution in hydrogen-ion concentration occurred which marked the end of precipitation. On comparing the inflexion thereby produced with that in the neutralisation curve of chromic acid, it will be observed that it indicates the first stage of neutralisation of all the free chromic acid present in the solution, $KHCrO_4$ being formed. The reaction may be regarded as two simultaneous reactions : first, the gradual hydrolysis of the thorium salt, thus :

$$ThCl_4 + 4H_2O \rightarrow Th(OH)_4 + 4HCl,$$

and, secondly,

$$4HCl + 4K_2CrO_4 \rightarrow 4KCl + 4KHCrO_4.$$
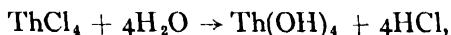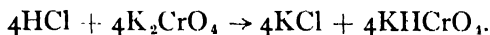
As stated above, it would be expected that thorium hydroxide would show a negligible tendency to react with the small concentrations of hydrions which arise from the dissociation of hydrochromate ions. Yet the thorium hydroxide which was precipitated contained appreciable amounts of chromic anhydride. Two reasons may be offered : (*a*) co-precipitation of thorium chromate, and (*b*) adsorption of chromic anhydride, through chemical forces at play between the weak base, thorium hydroxide, and the weak acid, $HCrO_4'$. The precipitates, apart from being yellow, resembled thorium hydroxide and appeared to contain no crystalline thorium chromate. Thorium chromate is much more soluble

than the hydroxide, and seeing that the thorium- and chromate-ion concentrations were insufficient to produce a precipitate of the normal chromate before the hydroxide precipitation pH was attained, it appears improbable that the basic chromate contained any normal chromate. The large chromic anhydride content of the basic precipitate was probably caused by a process akin to adsorption in which the chemical tendencies of the weak acid and the weak base played an important part.

An approximate estimate of the composition of the precipitate may be obtained from the titration curve. Precipitation was complete when 53 c.c. of M/20-potassium chromate had been added, *i.e.*, an amount corresponding to the mid-point of the inflexion. If thorium hydroxide alone had been precipitated, then, as shown by the previous equations, 4 molecules of potassium chromate to 1 molecule of thorium chloride would have been required, or 80 c.c. in the titration ; as compared with 2 molecules, or 40 c.c. of M/20-potassium chromate, if the normal chromate had been formed. But actually 53 c.c. were required, and therefore by alligation the basic chromate precipitate must have contained $27Th(CrO_4)_2,13Th(OH)_4$, or $ThO_2,1·35CrO_3$. The precipitate contained 54·55 per cent. of ThO_2 and 28·47 per cent. of CrO_3, and therefore agreed with the formula $ThO_2,1·38CrO_3,4·57H_2O$, which is similar to that suggested by the curve.

Aluminium.—Precipitation began when 5 c.c. of M/10-potassium chromate had been added, the pH attained being that required for the precipitation of aluminium hydroxide. At first, the precipitate was white basic aluminium sulphate, but gradually became yellow and contained some chromate (compare Gröger, *Ber.*, 1902, **35**, 3420). The main inflexion occurred and precipitation became complete when between 32 and 35 c.c. were added. The precipitate was gelatinous and contained chromate, much of which could be removed by washing.

The experiments of Gröger on the solubility of aluminium hydroxide in chromic acid solutions throw some light on the reactivity of the acid. He found that the number of molecules of chromic anhydride required to hold 1 molecule of alumina in solution varied from 4·46 to 5·02, and therefore concluded that both aluminium chromate and dichromate were capable of existence in solution. The explanation lies in the mode of dissociation of chromic acid. The first stage of the ionisation permits of the ready solution of aluminium hydroxide, thus $Al(OH)_3 + 3H_2CrO_4 \rightleftharpoons Al(HCrO_4)_3 + 3H_2O$, which requires 6 molecules of CrO_3 to 1 molecule of Al_2O_3, but the amount of hydrions produced in the second stage of the dissociation

will depend on the concentration of chromic acid used. If it be large, the great concentration of hydrochromate ions will tend to suppress the second stage of dissociation and consequently there will be proportionally fewer hydrions available for reaction than in a more dilute solution. Hence it is clear why Gröger required variable amounts of chromic acid which corresponded to somewhat less than 6 molecules.

Chromium.—Maus (*Pogg. Annalen*, 1827, **9**, 127) and later Storer and Eliot (*Proc. Amer. Acad. Arts Sci.*, 1862, **5**, 192) found that brown precipitates of basic chromium chromate, from which the chromic acid could be removed by repeated washing, were produced by the action of potassium chromate on solutions of chromium salt. The latter investigators stated that the abstraction did not stop when the precipitate had attained any particular composition, and, from an equation based on the molecular proportion of potassium chromate which they found necessary for precipitation, concluded that CrO_2 (*i.e.*, $Cr_2O_3 . CrO_3$) must have been formed first.

The titration curve shows that the factor which determined precipitation was the hydrogen-ion concentration, for when 26 c.c. of M 10-potassium chromate had been added and the *p*H had become 5·2, as compared with 5·34 found for the hydroxide, the basic chromate began to separate. The amount of potassium chromate required was 2·6 molecules to 1 molecule of chromate sulphate. As the point of precipitation is determined by the hydrion concentration, the amount of potassium chromate required appears to be a function of the concentration of the reactants. The *p*H change prior to precipitation was indicated by a line which was nearly straight, comparable with the section corresponding to the addition of the first equivalent (to 1 Cr) of sodium hydroxide, in the alkali titration curve (Fig. 125). The fact that 2 molecules of sodium hydroxide had to be added to 1 molecule of chromium sulphate before precipitation began was due to the peculiar property of tervalent chromium of forming " soluble basic salts," such that in a solution of the sulphate 1 molecule of sulphuric acid is in a state of loose combination which may perhaps be expressed by the equilibrium $Cr_2(SO_4)_3 + 2H_2O \rightleftharpoons (OH)_2Cr_2(SO_4)_2 \ldots H_2SO_4$, the looseness of the combination being indicated by the dotted line. This molecule of sulphuric acid, on its gradual release, reacted with two molecules of potassium chromate, thus :

$$H_2SO_4 + 2K_2CrO_4 = 2KHCrO_4 + K_2SO_4,$$
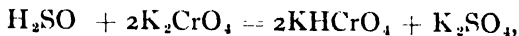
and the remaining 0·6 molecule of potassium chromate set up an

equilibrium with the hydrochromate ions so formed to produce the requisite hydrion concentration for precipitation.

The precipitates formed by treating chromium sulphate solution (as chrome alum) with varying proportions of potassium chromate, corresponding to 30, 60 and 90 c.c. in the titration, were analysed. After being freed from mother-liquor by suction and a little washing by decantation, the first precipitate was green and had the composition, omitting water content, $Cr_2O_3,0\cdot079CrO_3$, and was thus almost pure chromium hydroxide ; the second was brown and contained more chromate, $Cr_2O_3,0\cdot574CrO_3$; and the third, still more, its composition being $Cr_2O_3,0\cdot871CrO_3$.

Beryllium is another of the elements which form soluble basic salts, and this property appears to be reflected in the titration curve, the pH at which precipitation began not being attained until 24 c.c. of M/10-potassium chromate had been added, *i.e.*, 1·2 molecules for 1 molecule of beryllium sulphate.

The alkali curve (Fig. 124) shows a characteristic inflexion during the reaction with the first equivalent of sodium hydroxide ; precipitation occurred at pH 5·69 (given at the top of an inflexion), when 1·04 equivalents had been added. A similar inflexion occurred in the chromate titration curve and precipitation began at pH 5·72, indicated by a point in a similar position. The equivalent amount of potassium chromate which produced this change was 2·4 times that of the alkali and consequently the change in hydrion concentration was due to reaction between a loosely bound equivalent of acid in the beryllium sulphate molecule and potassium chromate, hydrochromate ions being formed which eventually entered into equilibrium with the added chromate ions.

Bleyer and Moorman (*Z. anorg. Chem.*, 1912, **76**, 70 ; see also Orlov, *ibid.*, 1913, **79**, 365) found that the interaction of potassium chromate and beryllium sulphate in solution produced very highly basic chromate precipitates, the chromate content of which seemed to increase slightly with the amount of potassium chromate added. Thus with 2 molecules of potassium chromate to one of beryllium sulphate the precipitate contained $BeO,0\cdot036CrO_3$, and with 4 molecules of potassium chromate, $BeO,0\cdot07CrO_3$, some unattacked sulphate being present in each precipitate. Bleyer and Moorman, having found that chromic acid solutions saturated with beryllium hydroxide contained the two in equimolecular proportions, stated that beryllium chromate existed in solution. Solutions of strong acids saturated with beryllia are invariably basic, and, as shown by the titration curve of beryllium sulphate and sodium hydroxide (*loc. cit.*), the solution had to be rendered

basic to an extent shown by the formula $Be(SO_4)_{0.5}(OH)$ before precipitation commenced. Similarly, the proportions in Bleyer and Moorman's solutions show that they were basic to the same extent, *viz.*, $Be(HCrO_4)(OH)$, chromic acid being too weak in its second stage of dissociation to react with beryllium hydroxide to any appreciable extent.

Zinc.—Table 181 shows that the *p*H of precipitation of basic zinc chromate was 5·49 and therefore somewhat lower than that of the hydroxide, 7. The rapidity with which the *p*H changed during the addition of the first cubic centimetres of potassium chromate rendered it difficult to ascertain with any degree of precision the exact point at which the precipitate appeared. The precipitate was basic and consequently the hydrion concentration of the solution was controlled mainly by the equilibria between the liberated hydrochromate ions and chromate ions. Gröger's analysis (*Monatsh.*, 1904, **25**, 520) showed that the precipitates obtained by treating zinc sulphate solutions with potassium chromate were indefinite and contained some sulphate, but the precipitates obtained from zinc chloride solutions were free from chloride, evidently due to the greater ease with which chlorides are hydrolysed. Varying amounts of potassium chromate were retained but were removable by washing.

An insoluble normal zinc chromate has been stated to exist by Schultze (*Z. anorg. Chem.*, 1895, **10**, 148) and Briggs (*ibid.*, 1908, **56**, 254 ; *J. Chem. Soc.*, 1929, 242). It was thought that, if a difficultly soluble chromate did exist, its solubility might be too large for it to be precipitated by double decomposition through the attainment of the *p*H at which the basic chromate separated, but that it might be precipitated from a chromic acid solution of zinc oxide by the gradual addition of potassium chromate so that the *p*H should be kept below that necessary for the precipitation of the basic chromate (compare Britton, *J. Chem. Soc.*, 1924, **125**, 1875). Indefinite basic chromates were always obtained ; *e.g.*, one air-dried precipitate, excluding the water content, corresponded to $ZnO,0.605CrO_3$, and another corresponded to $ZnO,0.462CrO_3$.

Gröger (*Z. anorg. Chem.*, 1911, **70**, 135) determined the solubility of zinc oxide in chromic acid solutions varying in concentration from 0·006 M. to 9·7 M. The number of molecules of chromic acid, H_2CrO_4, required to dissolve one molecule of zinc oxide varied continuously with increasing concentration of acid from 1·20 to 2·03, which led Gröger to conclude that the more dilute solutions contained both zinc chromate, $ZnCrO_4$, and zinc dichromate, $ZnCr_2O_7$, whilst the highly concentrated solutions

contained only zinc dichromate. The fact that approximately two molecules of chromic acid were required for the most concentrated acid solutions was due to the reaction having taken place between zinc oxide and the hydrions of the first dissociation, thus : $ZnO + 2H_2CrO_4 \rightarrow Zn(HCrO_4)_2 + H_2O$, the large concentration of hydrochromate ions having inhibited further ionisation and consequent reaction, whereas in the dilute solutions some of the hydrions from the second stage of ionisation became available for reaction, with the result that less than 2 molecules of chromic acid were required.

Cobalt and Nickel.—Reference may be made to Weil's proposal (*Bull. Soc. chim.*, 1911, **9**, 20) to use potassium chromate for the separation of cobalt from nickel. Although potassium chromate does not precipitate basic nickel chromate at room temperature, the titration curve shows that the hydrion concentration produced by addition of potassium chromate to a nickel salt solution is such that the basic salt is on the point of being precipitated. A method depending on such a small difference in solubility can give but a rough separation, for there will be a great tendency for the gelatinous basic cobalt chromate to carry down much nickel.

Rare Earths.—Yttrium.—Basic yttrium chromate began to be precipitated at the same *p*H as its hydroxide, but precipitation was far from complete and the precipitate was highly basic. The air-dried precipitate formed by the interaction of stoicheiometrical amounts of yttrium chloride and potassium chromate (40 c.c. of $M/10$-K_2CrO_4 in the titration) solutions contained the formula $Y_2O_3,1\cdot30CrO_3$. The filtrate from this precipitate was treated with more potassium chromate, and the new precipitate was still more basic and contained $Y_2O_3,0\cdot93CrO_3$.

Neodymium and Samarium.—These two elements form well-defined but comparatively insoluble chromates (Britton, *J. Chem. Soc.*, 1924, **125**, 1875) ; the power of these earths to unite with chromic acid in its two stages being, no doubt, due to the small solubility of the salts formed, rather than to the strength of the bases. The solubilities of praseodymium chromate and lanthanum chromate are so small that when potassium chromate is added to the respective salt solutions the conditions requisite for the precipitation of the normal chromates are obtained before the hydroxide *p*H is reached. This is not so with neodymium and samarium chromates, for they are suffi.:ently soluble to allow the *p*H at which the hydroxide is precipitated to be attained before the respective solubility products of the chromates are exceeded, and consequently basic chromate precipitates are produced.

When neodymium nitrate solution was treated with potassium chromate, a flocculent precipitate was obtained which on microscopic examination was seen to contain crystalline needles similar to those of the normal chromate. The following precipitates were so obtained : (1) $Nd_2O_3,2\cdot64CrO_3,9\cdot02H_2O$, and (2) $Nd_2O_3,2\cdot23CrO_3,7\cdot88H_2O$. The fact that precipitation began at pH 6·48 instead of at 7·0, coupled with the nature of the precipitates and the relatively high CrO_3 content, indicates that the formation of these precipitates constitutes a comparatively rare example of the co-precipitation of the crystalline normal salt and an indefinite basic salt.

Samarium chromate has a greater solubility than neodymium chromate and does not appear to be precipitated with the basic chromate. As the titration curve shows, the basic chromate was precipitated at pH 6·55, which was somewhat lower than the hydroxide pH. It was yellow and flocculent and when dried and examined under the microscope appeared to be entirely amorphous. Its separation was partial. The air-dried precipitate from the titration contained 25·1 per cent. CrO_3 as compared with 37·84 per cent. in $Sa_2(CrO_4)_3,8H_2O$.

II. Basic Borates.

Electrometric titrations were carried out at 18° with 0·05 M.-borax solution and salt solutions, which were so chosen that the precipitation reactions could be studied over as wide a range of hydrogen-ion concentration as possible. Details of the solutions used and the pH's at which precipitates first appeared are given in Table 182.

TABLE 182

PRECIPITATION OF BASIC BORATES

Solution (100 c.c.).	Precipitation of Basic Borate began : pH.	Precipitation of Hydroxide began : pH.	Precipitation.
0·01 M.-ZrCl₄	4·07	1·86	Complete
0·01 M.-ThCl₄	4·70	3·51	,,
0·0067 M.-Al₂(SO₄)₃	4·14	4·14	,,
0·01 M.-Cr₂(SO₄)₃,K₂SO₄ . . .	5·25	5·34	,,
0·02 M.-BeSO₄	5·72	5·69	,,
0·02 M.-ZnSO₄	5·27	7·0	,,
0·02 M.-MnCl₂	8·82	8·43*	} Partial
0·02 ,,	—	8·85	
0·02 M.-MgSO₄	—	10·49	None

The titration curves are given in Fig. 134, the arrows showing the points at which precipitation began.   The top curve in the diagram represents the titration of 100 c.c. of 0·02 M.-manganous chloride with 0·1018 M.-sodium metaborate.
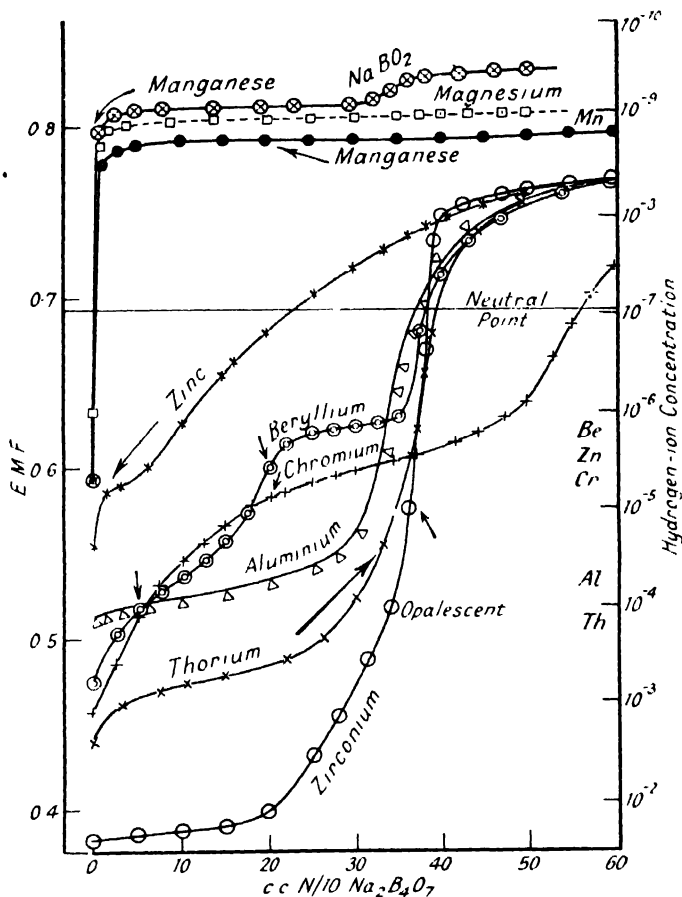
FIG. 134.—Precipitation of Basic Borates.

Table 182 shows that, except in the case of zirconium and thorium, addition of borax solution did not cause precipitation to begin until the pH at which the hydroxide is precipitated had been attained.   The titration curves in Fig. 134, apart from that of zinc, are similar in shape to those representing the alkali titrations.

Moreover, those curves which correspond to precipitation taking place in the acid zone show that the amounts of $N/10$-borax solution which caused the solutions to become alkaline, precipitation having become complete, were approximately the same as those required in the sodium hydroxide titrations. It appears, therefore, as far as the weaker bases are concerned, that sodium pyroborate has simply a hydrolysing action in precipitating the hydroxides, and in fact behaves as if no borate were present at all. The hydroxides which were precipitated contained some unattacked acid radical of the original salt, as may be seen from the amounts of $N/10$-borax required to render the solutions neutral, if it be assumed that the borate radical did not enter into combination. Thus in the zirconium titration, 38·5 c.c. were required as compared with the theoretical amount, 40 c.c. ; thorium, 38·0 instead of 40 c.c. ; aluminium, 36·0 instead of 40 c.c. ; chromium, 55 instead of 60 c.c. ; and beryllium, 37·6 instead of 40 c.c.

Provided that no insoluble normal borates are formed, it follows on theoretical grounds that boric acid, HBO_2, with its exceptionally small dissociation constant, is incapable of producing hydrogen-ion concentrations large enough to cause dissolution of any of the hydroxides which are precipitated at pH less than 7. Boric acid behaves as a monobasic acid. If 5×10^{10} be taken as an average value of $K = [H^{\cdot}][BO_2{}']/[HBO_2]$, it follows that in a $M/10$-boric acid solution the hydrogen-ion concentration is $10^{-5\cdot2}$, and $10^{-5\cdot6}$ in a $M/100$-solution. The hydroxides of beryllium, chromium, aluminium, thorium, and zirconium are all precipitated at pH values equal to, or less than 5·69, and consequently the hydrion concentrations of $M/10$- and $M/100$-solutions of boric acid are too small to have any solution effect on these hydroxides. Taking the case of beryllium hydroxide, which is precipitated at the highest pH of the series under consideration, in order that the reaction $Be(OH)_2 + 2HBO_2 \rightleftarrows Be(BO_2)_2 + H_2O$ may proceed, water must be formed and therefore the product of the concentration of hydroxyl ions due to beryllium hydroxide, viz., $10^{-14\cdot14}/10^{-5\cdot69} = 10^{-8\cdot45}$, and that of the hydrions from the boric acid, about $10^{-5\cdot2}$, must exceed K_w. In this case it is $10^{-13\cdot9}$, and only just exceeds K_w, and consequently beryllium hydroxide may perhaps be expected to exhibit the slightest tendency to dissolve. Any dissolution, however, would cause an increase in the concentration of $BO_2{}'$ ions, which would depress the ionisation of boric acid and so prevent further solution. Boric acid does not dissolve either of these bases to any perceptible extent.

The hydrogen-ion concentrations of the solutions at the end of these titrations are such as would be given by borate mixtures

comprising the total quantity of boric acid added and the alkali in excess of that required for the precipitations, and therefore confirm the view that no boric acid, or relatively little, was contained in the precipitates.   Thus in the titrations of zinc, beryllium, aluminium, thorium, and zirconium, it will be seen from Fig. 134 that the hydrion concentration when 60 c.c. of $N/10$-borax had been added was $10^{-8.3}$ in each case.   By subtracting the 40 c.c. of $N/10$-sodium hydroxide which were neutralised during the precipitations, it is found that the solutions contained alkali equal to 20 c.c. of $N/10$-sodium hydroxide and boric acid equal to 120 c.c. of $N/10$-HBO_2, the boric acid having been one-sixth neutralised. The pH of a 0·2 N-solution of boric acid neutralised to the same extent is 8·29, and as the variation in pH produced by the difference in concentration of the two solutions is very small, it will be seen that the agreement is sufficiently good.

Although the changes in hydrion concentration which took place in the acid zone of the titrations are almost identical with those which were obtained when the precipitant was sodium hydroxide, in the case of the two weakest bases, zirconia and thoria, the pH's of precipitation do not compare favourably with the corresponding hydroxide pH's.   Zirconium hydroxide is generally precipitated at a pH somewhere on the very slightly inclined part of the curve.   In the precipitation of zirconium chloride solution with sodium hydroxide (p. 79) the pH was 1·86, but in the present titration the solution remained perfectly clear until the inflexion in the curve had been passed and the pH had become 4·06 ; opalescence then appeared.   This was when 3·4 atoms of chloride of the zirconium tetrachloride had been replaced by hydroxyl groups and, notwithstanding its highly basic nature, the solution had remained perfectly clear.   With thorium chloride the effect was similar ; the solution remained quite clear until 3·3 atoms of chloride had been replaced and the curve had begun to incline, the pH being 4·70 instead of 3·51 obtained by using alkali.   Hence it appears that the boric acid was having some restrictive influence on the growth of the particles.   It is probable that the tendency, although very slight, which boric acid may have to combine with thoria and zirconia exerts its greatest influence just at the point where the hydroxide or basic salt is about to pass into colloidal solution prior to precipitation.   If this be the case, it seems reasonable that the boric acid, in trying to react with the nascent hydroxide, tended to keep it in solution by impeding the growth of the particles.   Two experiments were made to determine whether the delayed precipitation from a thorium chloride solution whose pH is that at which precipitation normally takes place is a matter of time.

To thorium chloride solutions of the concentration used in the titration were added amounts of borax equal to 2 and 3 equivalents ; in neither case did a precipitate separate during a period of several weeks.

In the chromium titration the solution became green on addition of the borax and precipitation occurred when 21·9 c.c. of N, 10-solution had been added, or 1·09 equivalents for each atom of chromium.

The beryllium curve again is similar to the alkali curve, and precipitation was also delayed until 21·9 c.c. (− 1·09 equivalents to 1 atom of Be) had been added.

The zinc curve shows hydrogen-ion changes which were due mainly to equilibria which must have been set up between borate ions and boric acid.

The incomplete precipitation which took place from M/50-manganous chloride solution will be understood when it is remembered that the pH of N 10-borax itself, $viz.$, 9·11, is only slightly greater than the pH at which manganous hydroxide is precipitated. Table 182 gives two pH values for manganous hydroxide ; the one marked with an asterisk is low, probably on account of oxidation of manganous hydroxide, and the other, which is approximately correct, was extrapolated from the alkali titration curve. In the borax titration the precipitate did not appear until 20 c.c. of N, 10-borax had been added and pH 8·82 attained. The precipitate was white and remained dispersed until 50 c.c. had been added, but, unlike the hydroxide, it did not immediately turn brown through oxidation. It readily did so when washed. (It is this protective action which is conferred on manganous hydroxide by union with some boric acid which makes the substance of use as a " drier " in paints and varnishes.) The fact that it was precipitated at the hydroxide pH suggests that the white precipitate was basic, and not manganous borate as was stated by Hartley and Ramage ($J. Chem. Soc.$, 1893, **63**, 133). The precipitate produced by the action of N, 10-borax on M 50-manganous chloride solution was both indefinite and basic and contained $MnO,1·47HBO_2$. In the titration of M 50-manganous chloride with 0·1018 N-sodium metaborate, the precipitate appeared when 1 c.c. of precipitant had been added and the pH had become 8·77. This precipitate was, like the hydroxide, quickly oxidised and was strongly basic.

Laurent ($Comp. rend. Trav. Chim.$, 1850, **6**, 33) observed that manganous salt solutions were not precipitated with potassium hexaborate. It will be seen from the hydrogen-ion concentrations of the various " buffer " mixtures that the pH of a boric acid

solution, a third of which has been neutralised with alkali and which thus corresponds to Laurent's reagent, is about pH 8·7, which just falls below the pH at which the hydroxide is precipitated. When, however, the borate solution is added to a manganous salt solution, some of the alkali is neutralised and the pH falls a little further below 8·7.

According to Gmelin-Kraut (*Handbuch anorg. Chem.*, 1908, iii, [2], p. 324), Berzelius found that when a magnesium salt had been added to a manganous salt solution, borax failed to give a precipitate. Neutral salts, such as sodium chloride, sodium sulphate, calcium chloride and potassium chloride, also produce this effect, but to a lesser extent ; *e.g.*, a solution from which precipitation had been prevented with magnesium sulphate remained clear on standing, whereas by using either potassium chloride or any of the other salts brown precipitates appeared after 12 hours. Precipitates obtained by means of borax may be forced back into solution by the addition of these salts. Since the highest pH that could be produced by borax solutions was far removed from the precipitation pH of manganous hydroxide, it appeared that the behaviour of these salts in preventing precipitation of basic manganous borate lay in their power to diminish the pH below that necessary for precipitation. For example, when 10 c.c. of a saturated solution of magnesium sulphate were added to 100 c.c. of N/10-borax solution whose initial pH was 9·11, the pH fell to 8·58 ; with 40 c.c., pH was 8·10 ; and with 50 c.c., 8·06. The effect of potassium chloride was not so marked. The addition of much potassium chloride to a N/10-borax solution depressed the pH only from 9·11 to 8·82—a value, it will be noticed, corresponding to incipient precipitation.

The dotted curve shows the changes produced in hydrogen-ion concentration during the addition of N/10-borax solution to a M/50-solution of magnesium sulphate. No precipitate was obtained, for the pH of the borax solution was below that, 10·49, requisite for the precipitation of magnesium hydroxide. Borax produces in the boiling solution a precipitate which redissolves on cooling. No precipitate was obtained with N/10-sodium metaborate solution, for although its pH was 10·85, the pH of the mixture became a little lower than the necessary value.

III. Basic Carbonates.

The hydrogen electrode titration method has been applied in a study of the relationships involved in the precipitation of basic carbonates. By using a plentiful supply of hydrogen in electrodes, which were efficient in ordinary solutions, potential differences

between them and the normal calomel electrode were obtained, in these carbonate titrations, which were readily reproducible and were unaffected by any liberated carbon dioxide. Table 183 gives
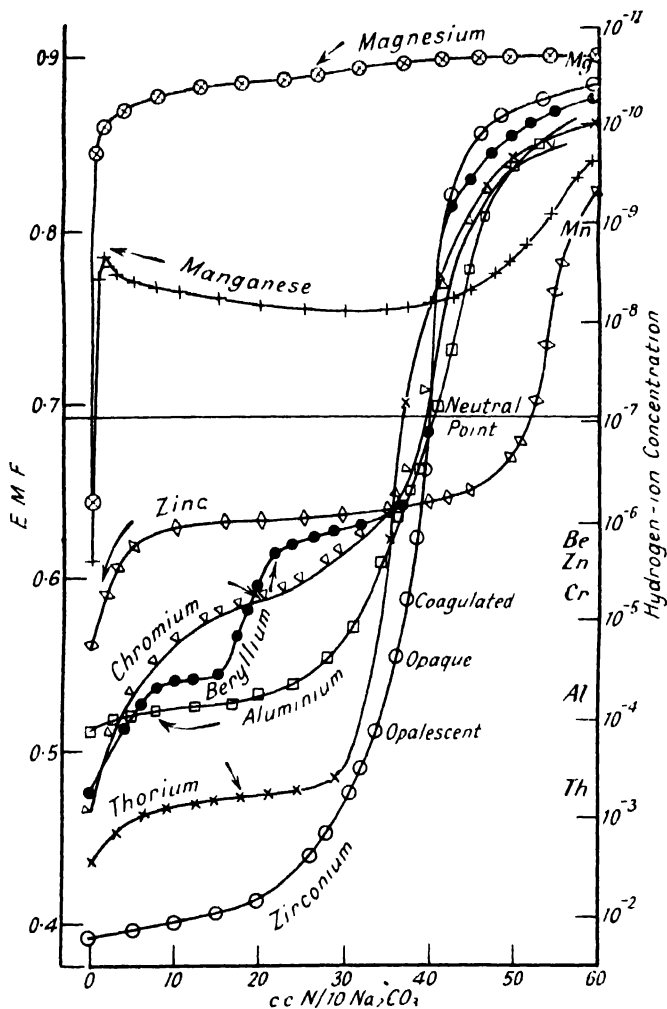
FIG. 135.—Precipitation of Basic Carbonates.

the particulars of the several titrations, and Fig. 135 shows the titration curves, the points at which precipitation began being again denoted by arrows. The sodium carbonate was decinormal in every case except in the chromium titration, when it was 0·166 N.

TABLE 183

PRECIPITATION OF BASIC CARBONATES

Solution (100 c.c.).	Precipitation of Basic Carbonate began. pH.	Precipitation of Hydroxide began : pH.	Precipitation.
0·01 M.-ZrCl₄	3·95	1·86	Complete
0·01 M.-ThCl₄	3·35	3·51	,,
0·0067 M.-Al₂(SO₄)₃	4·16	4·14	,,
0·01 M.-Cr₂(SO₄)₃,K₂SO₄	5·27	5·34	,,
0·02 M.-BeSO₄	5·70	5·69	,,
0·02 M.-ZnSO₄	5·30	7·0	,,
0·02 M.-MnCl₂	8·68	8·85	,,
0·02 M.-MgSO₄	10·54	10·49	Turbidity

The titration curves are of the same type as those obtained in the preceding hydrolytic precipitation titrations, and in every case but zirconium, precipitation began at hydrion concentrations equal or very nearly equal to those necessary for the corresponding hydroxides. N/10-sodium carbonate, unlike the reagents used in the previous titrations, when added to the magnesium sulphate solution, produced an alkalinity corresponding, but only just, to the pH at which the hydroxide is precipitated, which did not occur until 27 c.c. had been added. The precipitate formed even after 100 c.c. of sodium carbonate had been added did not amount to more than a slight turbidity.

The stoicheiometrical quantity of sodium carbonate required for simple double decomposition was equivalent to 40 c.c. of N/10-sodium carbonate, except in the case of chromium, where it was 36 c.c. The curves for zirconium, thorium, aluminium, beryllium, and chromium show that the mother-liquors became alkaline when approximately theoretical quantities of sodium carbonate had been added. The hydrion concentrations at the end of the titrations, although differing somewhat owing to the escape of different amounts of carbon dioxide during the precipitations, were such as would be produced by mixtures of sodium bicarbonate and carbonate compare Prideaux, ("Theory of Indicators," p. 299 ; Auerbach and Pick, *Arb. K. Gesundheitsamt.*, 1911, **38**, 243). The changes in hydrion concentration which took place during the precipitation of the basic carbonates from solutions whose hydrogen-ion concentrations were greater than 10 [6] were scarcely at all affected by the carbon dioxide that was liberated. The carbon dioxide set free during the precipitation of basic zinc carbonate, however, had so marked an effect on the hydrogen-ion concentra-

tion that the inflexion corresponding to the formation of sodium bicarbonate from the liberated carbon dioxide and the added sodium carbonate did not occur until 54 c.c. of the latter had been added.

The curve for manganese shows that the addition of N/10-sodium carbonate, after the first 2 c.c., produced a diminution in pH, which reached a minimum at pH 8·2 when 30 c.c. had been added. The precipitate appeared when 1·4 c.c. had been added and pH 8·68, *i.e.*, nearly the hydroxide pH, had been attained. The precipitate first formed was basic, as may be seen from the curve, which shows that more than 40 c.c. of sodium carbonate had to be added before the pH of sodium bicarbonate was attained, *viz.*, 8·7.* The precipitate, although basic, did not turn brown through oxidation by the air. It is remarkable that the increase in hydrion concentration which occurred during the titration did not cause the basic carbonate to re-dissolve. This, however, was a case of two precipitations, one of the basic carbonate due to the pH's ruling at the beginning and at the end of the reaction, and the other of the normal carbonate, which was precipitated when the hydrion concentration of the solution was enhanced. Sodium bicarbonate when added to a manganous chloride solution, preferably saturated with carbon dioxide, causes the precipitation of manganous carbonate only, for it cannot produce a sufficiently low hydrion concentration to enable the basic carbonate to separate from solution ; *e.g.*, the hydrion concentration of a manganous chloride solution was gradually reduced by the addition of a solution of sodium bicarbonate until the pH was 7·6, when a white precipitate of manganous carbonate began to form. Hence, in order to ensure the precipitation of the normal carbonate, the precipitant must be incapable of causing the pH to be attained at which the hydroxide is precipitated.

Normal zinc carbonate has been prepared. The titration curve shows that in order to precipitate this salt uncontaminated with basic carbonate a reagent must be used which, besides causing the solubility·product $[Zn^{··}][CO_3^{''}]$ to be exceeded, will maintain a hydrogen-ion concentration greater than that at which the basic carbonate would separate. Sodium bicarbonate with its pH of 8·7 would be useless, even though the carbon dioxide which would be set free during the precipitation would tend to increase the hydrion concentration. It would be necessary to have the solution saturated with carbon dioxide under a high pressure before

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* It may be calculated from Noyes's formula (*Z. physikal Chem.*, 1893, **11**, 495), by taking K_1 of carbonic acid to be 3×10^{-7} and K_2 $1·3 \times 10^{-11}$, that the pH of dilute solutions of sodium bicarbonate is about 8·7.

any addition of sodium bicarbonate.   Smith (*J. Amer. Chem. Soc.*, 1918, **40**, 883) has determined the solubility of zinc carbonate in solutions of carbon dioxide under pressures ranging from 4·12 to 40·6 atmospheres.   His results may be used to calculate the hydrogen-ion concentrations of the various solutions which, being in equilibrium with zinc carbonate, were just on the point of precipitating zinc carbonate, if it be assumed, as was done by Bodländer (*Z. physikal. Chem.*, 1900, **35**, 23), that metallic bases exist in carbonic acid solutions in the form of bicarbonates.   If zinc oxide exists as $Zn(HCO_3)_2$, the concentration of HCO_3' ions is equal to twice the concentration of dissolved zinc oxide, and, the extremely small concentration of hydrions arising from carbonic acid in its second stage of dissociation being neglected, it follows that $[H^*] = [H_2CO_3]K_1/[HCO_3'] = ([CO_2] - 2[ZnO]) \cdot 3 \times 10^{-7}/2[ZnO]$. It was thus calculated that the *p*H's of Smith's solutions varied continuously from 4·94 to 4·33.   Hence when the pressure of carbon dioxide is very high, the *p*H at which the normal carbonate is precipitated is much less than that at which the hydroxide is precipitated.

Mikusch (*Z. anorg. Chem.*, 1908, **56**, 365) determined the solubility of zinc oxide in carbon dioxide solutions in equilibrium with basic zinc carbonate.   By means of the above formula, it was found that the *p*H's of his solutions lay between 6·05 and 6·15. These hydrion concentrations, though somewhat lower than that at which basic zinc carbonate began to separate in the present titration, *viz.*, *p*H 5·3, happen to be those that obtained during the main course of the precipitation.   As zinc carbonate exists in equilibrium with hydrogen ions at a relatively high concentration, it follows that water will decompose zinc carbonate to give the less soluble basic carbonate.

The hydrogen-ion concentration which had to be attained in the magnesium titration before sodium carbonate produced a precipitate shows that, contrary to the statements of several workers, the precipitate was basic.   The solubility product of magnesium carbonate, $MgCO_3,3H_2O$, at 18° is 1·2 × 10^{-4} (Johnston, *J. Amer. Chem. Soc.*, 1915, **37**, 2014), and consequently, if complete dissociation be assumed, the solubility of magnesium carbonate in water is 1·1 × 10^{-2} mols. per litre.   The solubility of magnesium hydroxide, obtained from the solubility product, 2 × 10^{-9}, is 8 × 10^{-4} mols. per litre.   Hence, to precipitate the more soluble magnesium carbonate, a precipitant must be used which will supply the necessary carbonate ions without introducing the concentration of hydroxyl ions that causes the separation of magnesium hydroxide.   As magnesium hydroxide

is precipitated at pH 10·5, it is obvious that sodium bicarbonate (pH 8·7), even although added in large excess, cannot produce the corresponding concentration of hydrogen ions, and therefore cannot precipitate basic magnesium carbonate. It can, however, supply the carbonate ions which, provided that the magnesium salt solution is sufficiently concentrated, will cause magnesium carbonate to separate. Boussingault (*Ann. Chim. Phys.*, 1825, **29**, 285) found that sodium sesquicarbonate, $Na_2CO_3,2NaHCO_3$, also could be used for this purpose. The data of Auerbach and Pick (*loc. cit.*) show that the pH of such a mixture, decinormal with respect to carbonic acid, is approximately 9·9, which is just a little below the value required for the precipitation of the hydroxide.

No normal carbonates of chromium, beryllium, aluminium, thorium, and zirconium are known, and, as would be expected, the precipitates they form are highly basic. The shape of the beryllium titration curve appears to be peculiar to that element, and the precipitate did not appear until 22 c.c. ($= 1·1$ equivs. Na_2CO_3 to 1 mol. $BeSO_4$) of sodium carbonate had been added. In the chromium and thorium titrations, precipitation did not begin until 20 c.c. (1·85 equivs. to 1 Cr) and 18 c.c. (1·8 equivs.), respectively, of sodium carbonate had been added. As may be seen from Table 183, the precipitation which took place from thorium chloride solution with sodium carbonate was due to the attainment of the pH at which the hydroxide is precipitated and therefore the precipitate was basic. Chauvenet (*Comp. rend.*, 1911, **153**, 66), having found that the analysis of such a precipitate corresponded to the formula $ThO_2,CO_2,8H_2O$, stated that it was normal thorium orthocarbonate, $ThCO_4$, $8H_2O$, a salt of a purely hypothetical acid. In the case of the zirconium titration the curious effect noted in the borate titration was again observed, opalescence not beginning until 3·4 equivalents of sodium carbonate had been added and the relatively high pH of 3·95 had been attained. In the borate titration the pH was 4·06, and 3·4 equivalents of borax were required. As mentioned above, this phenomenon is believed to be due to suppression of the growth of the basic particles owing to a slight solvent action of the liberated weak acid.

IV. Basic Silicates.

Attention was directed (*J. Chem. Soc.*, 1927, 425) to the action of solutions of sodium silicate on typical metallic salt solutions. The precipitates thus obtained have received comparatively little attention, and the very few formulæ which have been assigned to them show that the ratio of silica to base is always higher than that

required to form the metasilicate. Some investigators have, how-
ever, mentioned that their precipitates contained free silica. The
difficulties inherent in the separation of a silicate precipitate, often
containing free silica, from its mother-liquor in anything approxi-
mating to the pure state (of which there is usually no criterion),
are so great that it is probable that the few analyses which have
been made convey no idea of the reaction which took place. We
see from the curve on page 315 that the acidic property of silicic
acid asserts itself only in alkaline solutions, and consequently it
would be expected that very little action could take place between
it and those hydroxides which are precipitated from acid solutions,
unless the substances formed by the interaction are extremely
insoluble. The view has been advanced, however, to account for
the acidity of " soil solutions," that complex aluminosilicic acids
exist in the soil through the interaction of aluminium hydroxide
and silica. If any such combination could take place, it is probable
that it would have some effect on the hydrogen-ion concentration
of the mother-liquor.

In its reaction towards strong bases silicic acid behaves quali-
tatively as a dibasic acid, the so-called metasilicic acid, H_2SiO_3.
Its neutralisation takes place mainly between pH 8 and pH 12.
Ray and Ganguly (*J. Physical Chem.*, 1930, **34**, 352) found that
hydrated silica begins perceptibly to dissolve at pH 8·5–9·5, and
that pH 6–9 is the range of minimum stability of silica sols.
Treadwell (*Trans. Faraday Soc.*, 1935, **31**, 297), however, stated
that 0·5 M.-SiO_2 sols gelatinise most rapidly at pH 5·8. Accord-
ing to Hazel (*J. Physical Chem.*, 1938, **42**, 409) colloidal silica
particles carry no electrical charge at pH 1, but acquire an in-
creasingly negative charge as the pH is raised (see also Hurd,
Frederick and Haynes, *ibid.*, 1938, **42**, 85 ; Batchelor, *ibid.*,
p. 575).

The changes in hydrogen-ion concentration were investigated
when solutions of sodium silicate and of metallic salts are allowed
to interact. The sodium silicate employed was prepared from
water-glass containing 2·16 molecules SiO_2 to 1 molecule Na_2O,
and was 0·1020 N with respect to sodium. The solutions used
are given in Table 184, together with the pH at which pre-
cipitation began, the amount of reactant which had to be added,
and the pH at which the respective hydroxides are precipitated.

The titration curves are plotted in Fig. 136, in which the begin-
ning of precipitation is marked by arrows. The amount of sodium
silicate required in each reaction such that the alkali was in a
quantity equivalent to the acid radical in 100 c.c. of salt solution
was 39 c.c. The curves lying beyond 39 c.c. illustrate the effect

TABLE 184

PRECIPITATION OF SILICATES

Solution Titrated (100 c.c).	Precipitation began at—		Hydroxide Precipitation at pH.
	pH	C.c. of Sodium Silicate.	
0·01 M.-ZrCl$_4$	3·98	35·0	1·86
0·01 M.-ThCl$_4$ . . .	3·50	30·0	3·51
0·0067 M.-Al$_2$(SO$_4$)$_3$ . .	4·04	5·0	4·14
0·02 M.-BeSO$_4$ . .	5·31	20·0	5·69
0·02 M.-ZnSO$_4$ . . .	5·25	1·0	7·0
0·02 M.-MnCl$_2$ . . .	7·35	1·0	8·41
0·02 M.-MgSO$_4$ . . .	9·50	1·0	10·49
0·02 M.-CaCl$_2$ . . .	10·07	3·0	—

of increasing amounts of sodium silicate on the hydrogen-ion concentration of the mother-liquor. The equation

$$Na_2O,2\cdot16SiO_2 + RCl_2 \rightarrow 2NaCl + RO,xSiO_2 \downarrow + (2\cdot16-x)SiO_2$$

shows that after the silicate RO,xSiO$_2$ had been precipitated by the 39 c.c., the mother-liquor comprised a sodium salt (chloride or sulphate), which through its very small concentration would have
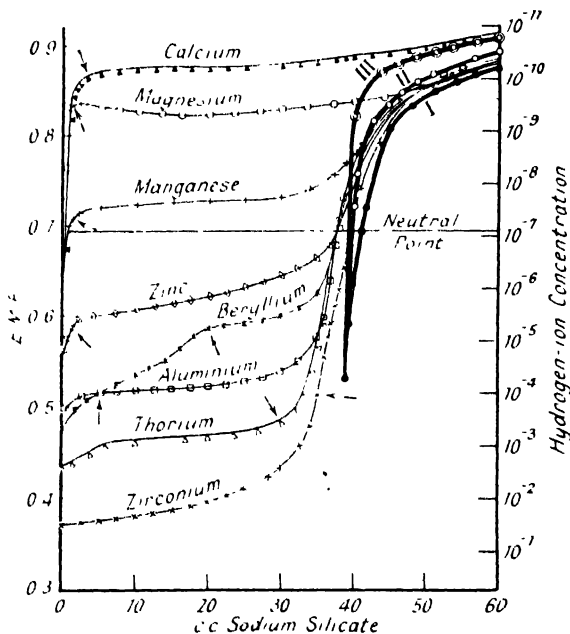
FIG. 136.—Precipitation of Basic Silicates

no measurable effect on the P.D., and a certain amount of silicic acid, which had escaped precipitation and would exert a buffering effect on the excess of sodium silicate. Some measure of the amounts of the silica which had remained in solution, and therefore of the amounts which had been precipitated with the metallic hydroxides, was obtained by following the changes in hydrogen-ion concentration when sodium silicate, of the same concentration as that used for the precipitations, was added to solutions having the volume attained when the precipitations had become complete, *viz.*, 139 c.c., and having the same concentration of neutral sodium salt as the original mother-liquors but different amounts of silica. Thus Curve I (Fig. 136) represents the course taken when sodium silicate was added to 139 c.c. of solution containing 39 c.c. of sodium silicate exactly neutralised (to methyl-orange) with hydrochloric acid ; it would therefore have been the curve obtained if the hydroxides alone had been precipitated and all the silica had remained in solution. Curve II shows the variation in hydrogen-ion concentration which would have been produced if the metasilicates of the metals had been precipitated, and the remainder of the silica had been left in solution ; whereas Curve III corresponds to the change which would have occurred if all the silica present in the 39 c.c. had been precipitated. Except for the calcium curve, those sections of the curves corresponding to an excess of sodium silicate lie between Curves I and II. Hence the amounts of silica carried down with the various precipitates were somewhat smaller than that necessary for the formation of normal metasilicates. Table 184 shows that the pH's at which the silicate precipitates of thorium and aluminium separated were also those at which the respective hydroxides begin to be 'precipitated. In the case of the zirconium titration, the silicate precipitate did not appear until pH 3·98 was reached, as compared with pH 1·86 for the hydroxide when precipitated from chloride solution. The curve in the acid zone shows that the change in hydrogen-ion concentration was similar to that which occurred in the precipitations of the hydroxide, basic borate, and basic carbonate. Precipitation was delayed until 3·59 equivalents of alkali had been added, whereas in the hydroxide precipitation opalescence appeared with 1·5 equivalents. Delayed precipitation was also noted with the basic borate and carbonate— 3·4 equivalents of reactant being required in each case, the pH's being 4·07 and 3·95, respectively. It is remarkable that the silica in the reagent should have impeded the precipitation until an almost identical pH, 3·98, had been attained. The other precipitate formed whilst the mother-liquor was still acidic was

that of beryllium ; this began to form at pH 5·31, which is slightly
lower than the hydroxide pH, 5·69.   As in previous work with
beryllium, the precipitate did not begin to form until 1·01 equiva-
lents of alkali, as sodium silicate, had been added.   The difference
between the two pH's may be due to the fact that the silicic acid
formed in the course of the reaction became very unstable on
approaching the neutral point.   The pH's at which the magnesium
and manganese precipitates began to form are considerably less
than those of the respective hydroxides.   The cause probably lies
in the insolubility of silicic acid, which cannot therefore retain
a base in solution until the hydroxide pH is reached.   This is
not the case with those precipitates which are formed in acid
solutions, for then the acid liberated by the hydrolysis of the
salts is sufficient to maintain solution until the corresponding
hydroxide pH is attained, or nearly so.   The interaction of
sodium silicate and a solution of calcium chloride produced a
curve which shows that when the stoicheiometrical amount of
alkali, as silicate, had been added, the alkalinity of the mother-
liquor was greater than that which would have been sent up if
all the silica in the sodium silicate had been removed from solu-
tion by the calcium precipitate and an excess of alkali had been
added instead of sodium silicate.   In the other reactions investi-
gated, it is probable that, owing to the great weakness of silicic
acid, very little or no combination took place between it and
the various hydroxides, the silica in the precipitates having been
the result of simultaneous precipitations.   It is, nevertheless sur-
prising that all the silica attached to those portions of the reagents
which were responsible for the precipitations was not itself com-
pletely precipitated with the hydroxides.   It is, of course, possible
that the excess of sodium silicate which was subsequently added
peptised some of the silica which had originally been precipitated.
The formation of silicate precipitates is probably the result of
the mutual coagulation of oppositely charged colloids through
the removal by neutralisation of the substances which tended to
stabilise or to peptise them, as found by Thomas and Johnston
(*J. Amer. Chem. Soc.*, 1923, **45**, 2532) in the case of the mutual
coagulation of a ferric hydrosol, peptised by ferric chloride, and
a silica sol, peptised by sodium silicate.

The precipitation of calcium silicate is, however, of quite a
different nature in that calcium hydroxide is fairly soluble in water
and is, moreover, sufficiently strong a base to react with silicic
acid.   The alkalinity of the solution was caused by the consider-
able hydrolysis of the calcium silicate, and the exceptionally high
pH of the solution after 39 c.c. of sodium silicate had been added

was apparently due to the withdrawal by the precipitate of more silica from the reagent, the precipitate thus containing more than 2 molecules of SiO_2 to 1 molecule of CaO.

In order to study the reactions (and consequent precipitations) between silicic acid and the alkaline earths, hydrogen-electrode titrations were carried out at 18° of solutions of 100 c.c. of 0·01112 M.-SiO_2 with each of the following solutions : 0·0447 N-calcium hydroxide, 0·0558 N-barium hydroxide, and 0·0359 N-strontium hydroxide. The solutions were prepared immediately before the titrations by neutralising sodium silicate solutions with hydrochloric acid, using methyl-orange, in order that they should contain the acid in a condition of maximum reactivity and that any diminution by ageing or by precipitation of the silicic acid should be avoided. These very dilute solutions though colloidal were quite clear. The titration curves, given in Fig. 137, show that precipitation of the silicates did not begin until appreciable amounts of alkaline-earth solutions had been added, and when approximately the same hydrogen-ion concentrations had been attained. Thus the compositions of the solutes when on the point of precipitation were $CaO,5·oSiO_2$; $BaO,5·o7SiO_2$; and $SrO,5·54SiO_2$; the respective pH's being 9·74, 9·72, and 9·90. In the case of the calcium and barium titrations marked inflexions occur between pH 10 and 11, but in the strontium titration an inflexion is scarcely perceptible. It was found that, in the calcium and barium reactions, these inflexions denoted the points when the silica and the whole of the added alkaline earths had become precipitated ; hence the precipitates must have been

$$CaO,3·o2SiO_2,xH_2O \text{ and } BaO,2·85SiO_2,xH_2O.$$
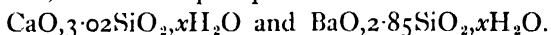
The hydrogen-ion concentrations of the solutions thereafter indicate that some further reaction took place between the precipitates and the added alkaline-earth solutions. The hydrogen-ion concentrations of the solutions prior to precipitation are comparable with those produced with sodium hydroxide (*vide* Fig. 173), showing that the condition in which the silicic acid is present in both the alkali and the alkaline-earth solutions is similar. It seems reasonable to suppose that the high proportion of silica retained in the solutions must be due to some colloidal micellar formation.

The amounts of silica found in "soil solutions" at any pH value are very small even when their calcium contents are comparatively high. This seems to be contrary to what might be expected from the foregoing observations. The absorption of carbon dioxide, however, is sufficient to decompose any calcium silicate solutions which may be formed.

The adsorption of alkaline earths by silica gel suspended in water was marked by a slow and gradual diminution in hydrogen-ion concentration. The curves showed a " buffer action," the extent of which depended ôn the amount of silica employed, commencing from pH 6·5, instead of the sharp change shown in Fig. 137, where the silica was not in great excess. The buffer action.of the silica gel is comparable with that which takes place when slaked lime is added to a soil, the reaction being usually between pH 6·5 and 9.
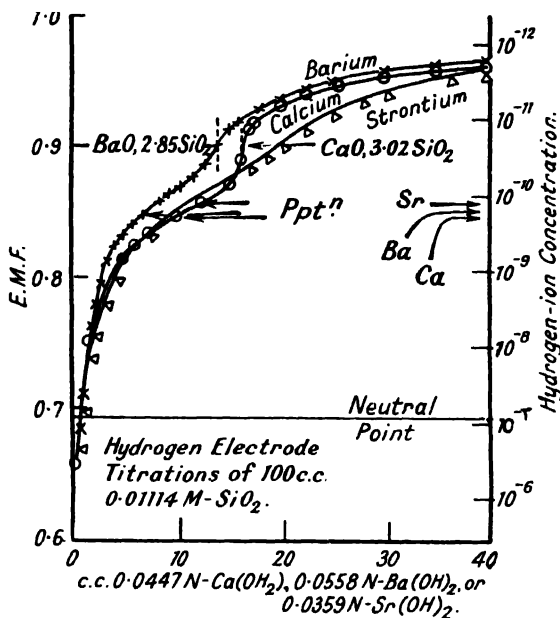
FIG. 137.—Precipitation of Alkaline Earth Silicates.

The action of alkalis and alkaline earths on aluminium hydroxide in forming soluble aluminates whose solutions are appreciably alkaline in reaction (see Figs. 123 and 124), coupled with the action of alkalis and alkaline earths on silicic acid, afford an explanation of the formation of permutites and zeolites. The compositions of most of the zeolites may be expressed by the general formula $RO,Al_2O_3,xSiO_2,yH_2O$, where R may represent one atom of a bivalent metal or two of a univalent metal, and $x = $ or > 2. For Gans' synthetic permutites x varied from 3 to 4. They were prepared by the action of alkali-metal aluminate solutions ôn silicic acid, and not by the action of alkali-metal silicate

on aluminium hydroxide.   It has been shown that the amounts of alkali or alkaline earth which dissolve aluminium hydroxide to form the soluble aluminate are approximately the same as those indicated by the formula $R^I AlO_2$, *viz.*, either 1 molecule $R_2^I O$ or 1 molecule $R^{II}O$ to 1 molecule Al_2O_3.   This happens to be the ratio found in zeolites.   Calcium aluminate solution on reacting with silicic acid, as either sol or gel, decomposes between pH 7 and 9 to give precipitates of calcium silicate (indefinite) and aluminium hydroxide, the aggregate composition of the precipitates being $CaO,Al_2O_3,xSiO_2,yH_2O$.

CHAPTER XXVI

THE PRECIPITATION OF SULPHIDES

THE study of the precipitation of metallic sulphides, with regard to the influence which hydrogen-ion concentration may have, has so far received very little attention. Perhaps the reason lies in the fact that the usual electrometric methods become invalidated owing to the poisoning effect of sulphides on the electrodes. Though the glass electrode has not yet been used for this purpose, it has been found to be capable of giving satisfactory results in the presence of sulphides in tanning liquors. The only work that appears to have been done has consisted of the precipitation of the sulphides, of zinc, cobalt and nickel from solutions that were buffered at various pH values (Fales and Ware, *J. Amer. Chem. Soc.*, 1919, **41**, 487; Haring and Leatherman, *ibid.*, 1930, **52**, 5135; Haring and Westfall, *ibid.*, p. 5141). Haring and his co-workers have shown that cobalt is completely precipitated with hydrogen sulphide at pH values equal to, or greater than, 3·9, whilst nickel requires the attainment of at least pH 4·5, provided that the solutions are heated to 90° C. Fales and Ware have shown that zinc sulphide is completely precipitated at pH 2 and above.

The following note will indicate the importance of pH in the precipitation of sulphides and especially in qualitative analysis.

Knox (*Trans. Faraday Soc.*, 1908, **4**, 43) has found that hydrogen sulphide ionises as a very weak acid in its first stage of dissociation, $K_1 = 9 \times 10^{-7}$, and as an exceedingly weak acid in its second, $K_2 = 1·2 \times 10^{-15}$. Hence as $pK_1 = 7·05$, we see from Chapter X that sodium hydroxide will react with hydrogen sulphide in solution between pH 5·05 and 9·05, thus

$$H_2S + NaOH \rightarrow NaHS$$

but will not commence to replace the second hydrogen until pH 12·92 is reached; pK_2 being 14·92, *viz.*,

$$NaHS + NaOH \rightleftharpoons Na_2S + H_2O$$

or ionically

$$HS' + OH' \rightleftharpoons S'' + H_2O.$$
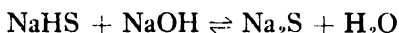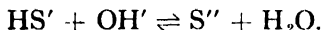
It is obvious therefore that solutions of sodium sulphide will be almost entirely hydrolysed and will contain sulphide-ions in

relatively low concentrations. This is even more so in the case of ammonium sulphide solutions. Knowing that

$$K_1 = [H^\cdot][HS']/[H_2S]$$

and
$$K_2 = [H^\cdot][S'']/[HS'],$$

we get

$$[S''] = K_1 \times K_2 \times \frac{[H_2S]}{[H^\cdot]^2}.$$

By using the formulæ given on page 229, Vol. I, the pH values of typical soluble sulphide solutions have been calculated. They are recorded in Table 185, together with the calculated concentrations of S′ ions, shown as $p[S'']$, where $[S''] = 10^{-p[S'']}$.

TABLE 185

	pH.	$p[S'']$
M-Na$_2$S	13·9	1·05
M-NaHS	10·5	4·4
0·1 M-NaHS	10·0	5·9
M-(NH$_4$)$_2$S	9·3	5·6
0·1 M-(NH$_4$)$_2$S	9·3	6·6
M-NH$_4$HS	8·1	6·8
0 1 M-NH$_4$HS	8·1	7·8
M-NH$_4$HS + excess NH$_4$OH . .	ca. 10·0	4·9
0·1 M-NH$_4$HS + excess NH$_4$OH.	ca. 10·0	5·9
H$_2$S (Satd. Solution)	4–5	14
M-HCl + H$_2$S	0	23
0·1 M-HCl + H$_2$S	1	21

The table shows that in acid solutions the sulphide-ion concentration is of the order of 10^{-23} g.-mol. per litre, whereas in the various ammonium sulphide solutions it ranges from 10^{-5} to 10^{-8}, the pH lying between 8 and 10. Despite these very small sulphide-ion concentrations, they are sufficient to bring about the precipitation of the various sulphides, though the sulphides that are actually precipitated depends on the pH of the solutions inasmuch as it determines the concentrations of the sulphide ions. This will be evident from Table 186, which has been prepared from the somewhat discrepant solubility product data recorded in Landolt's Tabellen.

The left-hand columns refer to the sulphides that are precipitated by passing hydrogen sulphide *into acidified solutions*, and those on the right to sulphides that undergo precipitation from solutions *of higher pH, preferably from pH 8–10*. It will be seen that the $p[S'']$ values corresponding to the former correspond to sulphide-ion concentrations much less than those of

TABLE 186

CALCULATION OF [S''] NECESSARY TO START PRECIPITATION
OF SULPHIDES FROM SOLUTIONS, 0·1 M. WITH RESPECT
TO METAL IONS

Solubility Product.	p[S''].	Solubility Product.	p[S'']
$[Pb^{..}][S''] = 10^{-27.4}$	26·4	$[Co^{..}][S''] = 10^{-23.5}$	24·5
$[Ag^{.}]^2[S''] = 10^{-48.8}$	46·8	$[Ni^{..}][S''] = 10^{-23.9}$	22·9
$[Cu^{..}][S''] = 10^{-44.1}$	43·1	$[Zn^{..}][S''] = 10^{-22.9}$	21·9
$[Cd^{..}][S''] = 10^{-28.4}$	27·4	$[Mn^{..}][S''] = 10^{-14.9}$	13·9
$[Hg^{..}][S''] = 10^{-48.7}$	47·7	$[Fe^{..}][S''] = 10^{-18.8}$	17·8

acid solutions saturated with hydrogen sulphide, *viz.*, *ca.* 10^{-23}, and they thus explain why these sulphides are precipitated from acid solutions. With the exception of the p[S''] referring to cobalt, which is certainly too high, those of the sulphides of nickel, zinc, manganese and iron are somewhat lower than 10^{-23}, and Table 185 reveals that in order to produce sufficiently high sulphide-ion concentrations to effect their precipitation it is necessary to use precipitants of higher pH values. The solubility products of the sulphides of zinc, cobalt and nickel, despite the fact that they are obviously approximate, explain why these sulphides may be precipitated from relatively acid solutions, as stated at the beginning of this chapter.

CHAPTER XXVII

PRECIPITATION OF NORMAL AND BASIC PHOSPHATES

The Precipitation of Phosphates.

As found on page 214, Vol. I, phosphoric acid behaves in its first stage of ionisation as a strong acid, $K_1 = 9.4 \times 10^{-3}$, in its second as a weak acid, $K_2 = 1.4 \times 10^{-7}$, and in its third stage as an extremely weak acid, $K_3 = 2.7 \times 10^{-12}$, so weak that its dissociation can only just be determined. It appears probable, from the very low order of magnitude of K_3, that the third hydrogen atom of phosphoric acid might be incapable of reacting with the majority of weak bases unless the phosphates happen to be very insoluble and the phosphate-ion concentrations of the mother-liquors are kept sufficiently large to exceed the solubility products without permitting the hydrogen-ion concentrations to become so small as to cause precipitation of the hydroxides. The author (*J. Chem. Soc.*, 1927, 614) studied the influence of K_3 in various precipitation reactions by means of the hydrogen and normal calomel electrodes in the usual manner. Two series of potentiometric titrations were made : the first comprising the reactions between solutions of phosphoric acid and strong bases, *viz.*, the hydroxides of sodium, calcium, barium, and strontium ; and the second series dealing with the action of trisodium phosphate, chosen because it involves the third stage of ionisation, on solutions of salts of typical metallic bases. A titration with lime water of phosphoric acid in a solution of sucrose was included in the first series in view of the discordant observations of Wendt and Clarke (*J. Amer. Chem. Soc.*, 1923, **45**, 881) and Hoffman and Gortner (*J. Physical Chem.*, 1925, **29**, 769) [see also Holt, LaMer, and Chown (*J. Biol. Chem.*, 1925, **64**, 509) and Farnell (*J. Soc. Chem. Ind.*, 1926, **45**, 343T)], and also on account of its importance in sugar refining (p. 294).

I. Phosphoric Acid and Alkaline Earths.

In Fig. 58 the titration curves at 20° C. of phosphoric acid with the alkaline earths are compared with one obtained by using sodium hydroxide. The solutions used were (1) 100 c.c. of 0.00965 M.-H_3PO_4 with 0.0558 N-$Ba(OH)_2$, (2) 100 c.c. of 0.00765 M.-H_3PO_4 with 0.0359 N-$Sr(OH)_2$, (3) 100 c.c. of 0.01024 M.-H_3PO_4 with 0.0447 N-$Ca(OH)_2$, and (4) 100 c.c.

of 0·01024 M.-H₃PO₄ containing 5 grams of sucrose with 0·0447 N-Ca(OH)₂. With the exception of the sodium hydroxide titration and the alkaline earth titrations up to the addition of the first equivalent, the E.M.F's recorded were not true equilibrium values, but were those indicated immediately after each addition of the reactant, for, as Wendt and Clarke observed in their lime-water titrations, the initial P.D's become smaller when the solutions stand for some time, through the slow reactions which take place between the precipitate and the added alkaline earth.

On comparing the alkaline-earth titration curves, up to the points corresponding to the beginning of precipitation, with that of sodium hydroxide, it will be seen that they cover almost identical ranges of hydrogen-ion concentration. In the lime-water titration precipitation was delayed until 1·53 equivalents (⇒ 35 c.c.) had been added and pH 6·72 was attained. On standing over-night, a solution of the same concentrations deposited an appreciable amount of precipitate and its pH fell to 5·98 ; in fact, precipitates were formed when solutions were allowed to stand which contained only just over 1 equivalent of calcium hydroxide. The delay in precipitation and the high initial pH were caused by neutralisation taking place immediately, whereas the precipitation from the supersaturated solution was a matter of time. Had neutralisation only taken place, the hydrogen-ion concentration would have been equal to

$$[\text{H}_2\text{PO}_4'] \times K_2/[\text{HPO}_4''] = (2 - n) \times 1\cdot4 \times 10^{-7}\,(n - 1),$$

where n is the number of equivalents of alkaline earth added, from which it follows that the pH of the calcium solution when on the point of precipitation should have been 6·91, which is slightly higher than the observed value, 6·72, the difference evidently being due to the precipitation reaction having proceeded to a small extent. The presence of sucrose in the phosphoric acid solution did not impede precipitation. In the baryta titration, 1·62 equivalents were required to start precipitation, which took place at pH 6·88 ; on standing over-night further precipitation occurred and the pH of the solution fell to 6·07. Strontium hydroxide solution produced a precipitate with 1·78 equivalents (38 c.c.) ; the pH was then 7·34, but it became 6·60 after standing over-night, more precipitate having separated. These titrations up to the point of precipitation consisted chiefly of neutralisation, for by calculation it is found that for neutralisation alone the pH should have been 7·07 in the barium titration instead of 6·88 observed, and 7·40 in the strontium titration instead of 7·34.

The precipitates first formed were the monohydrogen phos-

phates, $M''HPO_4$, which by the addition of more alkaline earth became converted into the normal phosphate, $M_3(PO_4)_2$. The inflexion in the baryta-titration curve occurred during the addition of the third equivalent, and therefore the precipitate was a mixture of di- and tribarium phosphates, whereas in the strontia curve the inflexion was not produced until the third equivalent had been added, showing that the precipitate was the normal strontium phosphate. The final inflexion in the calcium hydroxide titration occurred when the third equivalent had been added, suggesting that at that stage the precipitate was tricalcium phosphate. It will, however, be observed that further additions of lime water did not cause as great an increase in pH as in the other titrations. This was due to the adsorption by the calcium phosphate of some calcium hydroxide thus rendering the phosphate basic. Bassett (*J. Chem. Soc.*, 1917, 111, 620) found that one molecule of tricalcium phosphate can adsorb one-third of a molecule of calcium hydroxide to form " hydroxyapatite," $3Ca_3(PO_4)_2,Ca(OH)_2$; he believes that this is the calcium phosphate which can permanently exist in the soil under ordinary conditions.

The variation in hydrogen-ion concentration, which occurred in the lime-water reaction just after two equivalents had been added, is remarkable in that the addition of more reactant actually caused an increase in the concentration of hydrogen ions. It appears probable, therefore, that the added calcium hydroxide reacted with the dicalcium phosphate remaining in solution causing precipitation of the tricalcium salt, and in so doing it also decomposed the supersaturated solution, precipitating some dicalcium salt and possibly a little of the normal salt in accordance with the equation suggested by Wendt and Clarke :

$$4CaHPO_4 = Ca_3(PO_4)_2 + Ca(H_2PO_4)_2.$$

The pH data calculated from the phase-rule data of Bassett (*vide infra*) show that both the di- and the tri-calcium phosphates attain equilibrium with liquid phases whose pH's are about 5·5 through equilibria involving H_2PO_4' and HPO_4'' ions, the former being in considerable excess. It would be expected, therefore, that a pH of 5·5 would represent the lowest value to which this downward inflexion could attain, and it is interesting to find that this is about the value shown by Wendt and Clarke's curve. The higher pH obtained by the author was due to insufficient time being allowed for the attainment of final equilibrium. The earlier appearance of the inflexion in Wendt and Clarke's curve was due to the precipitation of the two phosphates of calcium. They found, by allowing 10 days for the attainment of equilibrium, that the curve became

rectilinear during the addition of the greater part of the second and third equivalents of calcium hydroxide, and indicated hydrogen-ion concentrations varying from pH 5·5, when a little more than the first equivalent had been added, to pH 6·0 at 2·5 equivalents. This is as would be expected from a consideration of Bassett's work (*vide infra*).   Farnell obtained similar results by boiling the solutions and cooling to 20° before measuring the pH.   By allowing the solutions to stand over-night in stoppered bottles, the author found that the change in hydrogen-ion concentration was gradual and varied, the final values being pH 5·98 at 1·53 equivalents to pH 6·52 at 2·5 equivalents.   These precipitations had not, however, become complete.

The titration curve of phosphoric acid in presence of sucrose given in Fig. 58 shows that sucrose acts as a buffer in preventing an increase in hydrogen-ion concentration.

The considerable amount of supersaturation, with its consequent effect on the hydrogen-ion concentration, which occurs when alkaline earths are added to phosphoric acid solutions, renders it difficult to ascertain, by means of a titration method, when a precipitate begins to separate.   The pH at which calcium begins to separate as a phosphate is of some importance in the chemistry of soils, and therefore certain data relating to the ternary system $CaO—P_2O_5—H_2O$ obtained by Bassett (*J. Chem. Soc.*, 1917, **111**, 624 ; *Z. anorg. Chem.*, 1908, **59**, 1) at 25'' and by Cameron and Bell (*J. Amer. Chem. Soc.*, 1905, **27**, 1512) have been studied with respect to the stage of neutralisation of the phosphoric acid in the liquid phases ; then, either by comparison with the neutralisation curve (Fig. 58), or by calculation, an approximate estimate has been made of the hydrogen-ion concentrations of the liquid phases in equilibrium with solid phases containing varying amounts of phosphate.   Table 187 was compiled from Bassett's data.

It will be seen from the table that those liquid phases which contained 0·149 per cent. $P_2O_5(= 0·02 M.-H_3PO_4)$ or less, as a rule, contained calcium hydroxide sufficient to neutralise about 5 per cent. of the second stage, giving hydrogen-ion concentrations of the order of $10^{-5.5}$.   The amount of lime became in excess of 2 equivalents for liquid phases containing less than 0·00613 per cent. $P_2O_5(= 0·0009 M.-H_3PO_4)$.   The solid phases which were more basic than $CaHPO_4$ are indicated by the molar ratio $PO_4 : CaO$, which is 0·67 for tricalcium phosphate and 0·60 for the substance, hydroxyapatite, $3Ca_3(PO_4)_2,Ca(OH)_2$.   The values of the ratio given in Table 148 suggest that the solid phases in equilibrium with the most dilute liquid phases were hydroxyapa-

tite, whereas the ratios corresponding to the more concentrated liquid phases fall, with one exception, between 0·66 and 0·95, proving that the solid phases were either mixtures of tri- and di-calcium phosphate, or possibly di-calcium phosphate in various stages of decomposition. The presence of two solid phases *in equilibrium* with variable liquid phases is incompatible with the

TABLE 187

ANALYSIS OF BASSETT'S DATA OF THE SYSTEM $CaO-P_2O_5-H_2O$

Per Cent. CaO.	Per Cent. P_2O_5.	Solid Phase.	Per Cent. Neutralised.*		pH.
1·181	3·613	$CaHPO_4$	82	(I)	3 approx.
0·826	2·387	,,	81	(I)	3 ,,
0·165	0·417	$\{CaHPO_4$ and $CaHPO_4, 2H_2O\}$	0·04	(II)	—
0·0696	0 178	$CaHPO_4, 2H_2O$	99·6	(I)	—
0·0617	0·149	,,	5·1	(II)	5·6
0·0507	0·121	,,	6·3	(II)	5·7
0·0485	0·119	,,	3·3	(II)	5·4
0·0427	0·105	,,	3·1	(II)	5·4
		PO_4/CaO in solid phase.			
0·0406	0·0980	0·76	5·1	(II)	5·6
0·0389	0·0947	0 79	4·1	(II)	5·5
0·0373	0·0897	0·95	5·5	(II)	5·6
0·0326	0·0777	0 62	6·4	(II)	5·7
0·0299	0·0727	0·67	4·4	(II)	5·5
0·0269	0 0607	0·66	12·4	(II)	6·0
0·0191	0·0465	0 70	4·1	(II)	5·5
0·0175	0·0423	0·71	4·9	(II)	5·6
0·0174	0·0414	0·69	6·5	(II)	5·7
0·0167	0·0405	0·69	4·6	(II)	5·5
0·0126	0·0332	—	96	(I)	—
0·0122	0·0302	0·66	2·4	(II)	5·2
0·00893	0·0196	0·63	12·0	(II)	6·0
0·00582	0 0134	0 62	10·1	(II)	5·9
0·00600	0·00613	0 62	4·9	(III)	11 approx.

* The Roman numerals (I), (II), and (III) relate to the first, second, and third stages of neutralisation of phosphoric acid, respectively.

phase rule, and it is considered that the conversion of di-calcium phosphate into the normal salt is very slow owing to the ionic requirements of the one being set up simultaneously with those of the other. Consequently, the solid phases may have been indefinite and unstable mixtures, although it appeared, as far as could be ascertained experimentally, that equilibrium had been established.

Action of Trisodium Phosphate on Metal Salt Solutions.

The variation in hydrogen-ion concentration which occurred at 20° when a N/10-solution of trisodium phosphate was added to 100 c.c. of the salt solutions (Table 188) was followed electrometrically. The E.M.F's were reproducible, except in the final stages of the chromium and magnesium titrations. Table 188 gives the pH's at which the phosphate precipitates began to separate, and, for purposes of comparison, the respective hydroxide pH's.

TABLE 188

Solution Titrated.	Phosphate pH.	Hydroxide pH.
0·02 M.-MgSO$_4$	9·76	10·49
0·0358 M.-CaCl$_2$.	7·00	—
0·02 M.-MnCl$_2$	5·76	8·43
0·02 M.-ZnSO$_4$	5·66	7·0
0·00667 M.-Cr$_2$(SO$_4$)$_3$, K$_2$SO$_4$	$\begin{Bmatrix}4·62\\5·65\end{Bmatrix}$	5·34
0·00667 M.-Al$_2$(SO$_4$)$_3$	3·79	4·14
0·02 M.-BeSO$_4$	3·41	5·69
0·01 M.-ThCl$_4$	2·72	3·51
0·01 M.-ZrCl$_4$	1·57	1·86
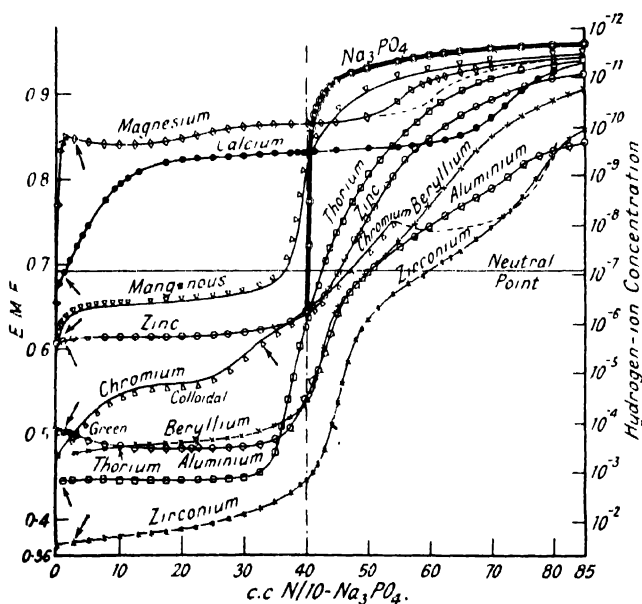
FIG. 138.—Precipitation of Normal and Basic Phosphates.

The curves showing the hydrogen-ion concentrations acquired when increasing amounts of trisodium phosphate had been added are given in Fig. 138. The amount of trisodium phosphate required to form the normal metallic phosphate was 40 c.c. in every case except that of calcium chloride, in which it was 71·6 c.c. The curve marked Na$_3$PO$_4$ was obtained by adding N/10-sodium phosphate solution to 140 c.c. of solution (i.e., the volume attained in the precipitation reactions when stoicheiometrical amounts of the phosphate solution had been added) containing an amount of sodium chloride equal to the amount of neutral salt formed in the precipitation reactions with 40 c.c. of sodium phosphate. It would therefore represent the variation in hydrogen-ion concentration on adding an excess of the reactant, if the pure normal phosphates had been precipitated, leaving in solution amounts of phosphate so small as to exert no " buffer action." The arrows denote the beginning of precipitation.

In no instance did the curve corresponding to an excess of the reactant coincide with this curve, the two nearest being those of manganese and calcium. The others are widely divergent. The pH data given in Table 188 show that the phosphate precipitates separated from solutions whose hydrogen-ion concentrations were greater than those requisite for the precipitation of the corresponding hydroxides ; and thus it appears that, whilst it may be possible to obtain the normal phosphates by the use of an amount of trisodium phosphate insufficient to give complete precipitation, yet as soon as sufficient reactant has been added to bring the pH of the solution to that necessary for the precipitation of the hydroxide, any metallic salt remaining in solution will then be precipitated, and, moreover, there will be a strong tendency for the precipitate to be decomposed. That some such reaction must have taken place is evident from the curves. The depression of the manganese and the calcium curves must have been caused by the " buffer action " of the added sodium phosphate on the HPO$_4$″ ions, which had been supplied to the solutions by the precipitates. The greater hydrogen-ion concentrations set up in the zinc, beryllium, aluminium, and thorium reactions were of the same magnitude as those produced in the second, and subsequently in the third, stage of neutralisation. Hence the precipitates must have decomposed to furnish the mother-liquor with H$_2$PO$_4$′ ions, some of which, by reacting with the added phosphate, became converted into HPO$_4$″ ions.

No inflexion occurred in the zirconium chloride reaction when the stoicheiometrical quantity of sodium phosphate had been added, though one appeared on the addition of a small excess. By com-

paring the range of hydrogen-ion concentrations produced during the addition of this excess with that obtained towards the end of the neutralisation of the first stage of phosphoric acid (Fig. 58), it will be seen that the equilibria which produce these relatively large concentrations of hydrogen ions involve some free phosphoric acid. This must have been liberated through the extreme weakness of zirconium hydroxide, with the result that a highly basic zirconium phosphate was precipitated, the formation of which might have been expected from the fact that zirconium chloride solutions are very considerably hydrolysed. Thus it was found (Britton, *J. Chem. Soc.*, 1925, **127**, 2133) that a freshly prepared solution of the concentration used in this titration was hydrolysed to the extent of 54 per cent., and consequently the free acid liberated an equivalent amount of phosphoric acid on reacting with trisodium phosphate. The middle point of the first inflexion (corresponding with the addition of 45 c.c., an excess of 5 c.c.) represents the stage when the liberated phosphoric acid had reacted with the added phosphate to form monosodium phosphate, in accordance with the equation $Na_3PO_4 + 2H_3PO_4 = 3NaH_2PO_4$, from which it follows that the excess of 5 c.c. reacted with twice the amount, *i.e.*, 10 c.c., of phosphoric acid. The total amount of phosphoric acid was equivalent to 40 c.c., and of this 13·3 c.c. corresponded to the first stage of dissociation. The amount of phosphoric acid which had escaped precipitation was therefore 10/13·3 of the quantity required for the normal phosphate of zirconium, and hence the composition of the precipitate might be represented as $6ZrO_2, P_2O_5$. The curve obtained on adding a further excess of the reactant, instead of being sharply inflected through pH 9 owing to the complete formation of disodium phosphate, showed that a considerable " buffer action" occurred between pH 6 and 10. It appears, therefore, from the expression

$$[H'] = K_2 . [H_2PO_4'] . [HPO_4'']$$

governing the hydrion concentrations during the second stage of neutralisation, that the precipitate itself, in being decomposed, must have exerted some buffering action by imparting to the mother-liquor a small but continuous concentration of H_2PO_4' ions.

The precipitation curve of aluminium phosphate is interesting in that the first addition of sodium phosphate caused an increase in the concentration of hydrogen ions, reaching a maximum at pH 3·43 with 17·5 to 20 c.c. The precipitate became very basic when an excess of sodium phosphate was added as shown by the comparatively large buffering effect—at 80 c.c. the pH was 9·41 ;

at 100 c.c., 10·02 ; at 120 c.c., 10·24 ; and at 140 c.c., 10·33. The hydrolysis of the precipitate into aluminium hydroxide was accompanied by its gradual dissolution in the sodium phosphate solution. Thus the solution became translucent with 80 c.c. and quite clear with 140 c.c. Reference to the hydrogen-ion concentration curve showing the action of alkali on aluminium sulphate solution (p. 76) indicates that sodium aluminate began to form when the pH became between 9 and 10. Hence it appears that the dissolution of the precipitate in an excess of sodium phosphate was due to the formation of sodium aluminate, the necessary free alkali being furnished by the trisodium phosphate through the exceptional weakness of phosphoric acid in its third stage of ionisation and the resulting hydrolysis of its sodium salt. The inability of disodium phosphate, when added in excess, to cause the precipitate to dissolve is due to the low pH which it sets up. An excess of this precipitant reduces the hydrogen-ion concentration considerably below that at which aluminium hydroxide becomes precipitable, causing the precipitate to hydrolyse. Thus Munroe (*Amer. J. Sci.*, 1871, (iii), **1**, 329) found that a precipitate, $AlPO_4,Al(OH)_3,2·5H_2O$, was obtained when an alum solution was treated with an excess of the disodium salt.

Although precipitation did not take place from the beryllium sulphate solution until 7·5 c.c. of sodium phosphate had been added, the delay was not accompanied by any great change in hydrogen-ion concentration. As mentioned above, the final beryllium precipitate was a basic phosphate. Bleyer and Müller (*Z. anorg. Chem.*, 1913, **79**, 263) assigned the formula $BeO,2Be_3(PO_4)_2,13H_2O$ to a precipitate similarly obtained. The effect of the soluble basic salt formation was not apparent in the beryllium sulphate reaction, which was very probably connected with the slight solubility of the beryllium phosphate originally precipitated. The influence, however, was marked in the chromium titration. At first the sodium phosphate merely caused the violet solution to turn green—a point of importance in connexion with the question of the colours of chromium salt solutions, and one which is always observed whenever a violet chromium salt solution is rendered basic. Simultaneously an appreciable decrease in hydrogen-ion concentration occurred until 12 c.c. (= 0·90 equiv. per atom of Cr) had been added, $pH = 4·62$, a cloudiness then being observed. For the next 10 c.c. the pH remained nearly constant, although the solution became more and more colloidal, and thereafter a steady rise in pH occurred, coagulation taking place at pH 5·65 with 32·5 c.c. (= 2·44 equivs.). The bulk of the precipitate was green and flocculent, but it con-

tained a small quantity of a violet crystalline precipitate, apparently the normal chromium phosphate. The delay in precipitation is significant, as also is the fact that when it took place the hydrogen-ion concentration of the mother-liquor was not very far from that at which chromium hydroxide is precipitated, *viz.*, *p*H 5·3. The diminution in hydrogen-ion concentration was gradual until 54 c.c. (= 4·05 equivs.) of sodium phosphate ⁎ had been added, *p*H = 8·07, at which stage the E.M.F's not only became very unsteady, but also showed a remarkable increase in hydrogen-ion concentration. The changes which took place immediately after the addition of each new amount of sodium phosphate are shown by the broken line. The hydrogen-ion concentration subsequently grew smaller, such that when 80 c.c. had been added the *p*H had become 9·71. Precipitation became complete just after the stoicheiometrical amount of sodium phosphate, 40 c.c., had been added. The change in *p*H with the excess of reactant shows that a basic phosphate had been precipitated, and the exceptional change after 4 equivalents of sodium phosphate had been added indicates that the precipitate underwent rapid hydrolysis.

The *p*H, 5·66, at which the zinc phosphate precipitate began to form was lower than that required by zinc hydroxide, *i.e.*, 7·0, but reference to the hydroxide precipitation curve shows that the *p*H during the main part of the precipitation was *ca.* 7, whereas the phosphate curve shows a somewhat lower *p*H, *viz.*, 5·7.

The E.M.F's recorded in the reaction with calcium chloride up to the addition of 7 c.c. of sodium phosphate tended to be low initially but slowly increased to steady values ; for larger volumes of sodium phosphate the voltages given primarily appeared to be reproducible. The stoicheiometrical amount of sodium phosphate was 71·6 c.c., and this, as seen from the curve, gave rise to a hydrogen-ion concentration which was represented by the point of inflexion corresponding to the completion of precipitation as the normal calcium phosphate. The greater part of the precipitation occurred between *p*H 9·5 and 10, and, as will be seen from the sodium hydroxide titration curve (Fig. 58), such a *p*H corresponds to equilibria involving a predominance of HPO_4'' and very few PO_4''' ions, thus $HPO_4'' + OH' \rightleftharpoons PO_4''' + H_2O$, which must have been given by the hydrolysis of the tricalcium phosphate. The difference between the *p*H's which prevailed in this reaction and that during the precipitation from phosphoric acid (p. 213, Vol. I) is due to the suppression of the hydrolysis in the latter case by the small amount of partly neutralised phosphoric acid present, whereas this was absent in the double decomposition.

The precipitation from the magnesium sulphate solution is of interest for two reasons.   Firstly, the inflexion indicating the end of precipitation did not appear when the stoicheiometrical amount of sodium phosphate had been added, *viz.*, 40 c.c., but occurred with about $1\frac{1}{2}$ times that quantity.   Secondly, the solution from which the precipitate had separated was even more alkaline than that in the calcium reaction, the pH at which the precipitate began to form being 9·76.   The exact incidence of the inflected part depended on the efficiency of agitation of the reaction mixture and on the time allowed before measuring the E.M.F.   The broken line was obtained by allowing longer time, and the inflexion began at 60 c.c., whereas the first curve was undergoing inflexion with that amount.   A pH of 9·76 must have been produced by the same kind of ionic equilibria as in the calcium phosphate precipitation, in which, however, there was a greater proportion of phosphate ions.   The amount of sodium phosphate required to effect precipitation suggests the reaction :

$MgSO_4 + Na_3PO_4 + H_2O = MgHPO_4 + NaOH + Na_2SO_4$,

but the fact that the pH remained almost stationary at 10 throughout the course of precipitation shows that the concentration of free alkali was relatively small.   The precipitate was $NaMgPO_4$, and it was therefore by its hydrolysis that the pH throughout its precipitation was determined.

The Effect of pH upon the Precipitation of $ZnNH_4PO_4$.

Satisfactory results were obtained by Ball and Agruss (*J. Amer. Chem. Soc.*, 1930, **52**, 120) in the determination of Zn as $ZnNH_4PO_4$ by precipitating within the range pH 6·4–6·9, the optimum being at pH 6·6.   The precipitate is not crystalline at pH values above 7·0 and is collected with difficulty, whilst below pH 5·1 and above pH 7·7 low results are obtained.

Note on the Phosphate Separation.

The observations made in the course of these electrometric titrations afford a satisfactory explanation of the procedure adopted in qualitative analysis for the removal of phosphates.   The phosphate precipitation pH's are functions of the concentrations of both the metallic and the phosphate ions, and the use of dilute solutions tends to keep the concentrations of both the bases and phosphoric acid comparatively small, and thereby fixes within narrow limits the pH at which the various phosphates are precipitated as the free acid is gradually neutralised and the solution made alkaline.   The hydrogen-ion concentrations which prevailed during the formation of the phosphate precipitates (Fig. 198) are

approximately those which would be set up if the phosphoric acid had been present in the solution and was subsequently neutralised with alkali. In the " basic acetate " method of removing phosphates, the solution, before treatment with ferric chloride solution, is buffered at about pH 5 by the acetic acid and an excess of either sodium or ammonium acetate. Fig. 138 shows that the only phosphates to be precipitated from solutions more acid than pH 5 are those of zirconium, thorium, aluminium, beryllium, and chromium. Ferric and stannic phosphates are also precipitated at low pH's. The phosphates and hydroxides which are precipitated from solutions of pH higher than 5 are those of zinc, manganese, calcium, and magnesium, to which should be added cobalt, nickel, strontium, barium, and many of the rare earths. It appears, therefore, that as the pH of the phosphate solution is raised to 5, the phosphates precipitated will be, first, ferric, then aluminium, and finally chromium, but if the quantity of phosphoric acid in the solution is inadequate to form any or all of these phosphates, then the acid will combine with the bases in the order in which they are precipitated, and consequently the hydroxides themselves may be precipitated. Hence, by having a quantity of these three bases, and preferably of ferric hydroxide, more than sufficient to combine with the total amount of phosphoric acid present, the phosphate will be completely removed without precipitation of the bases belonging to the subsequent groups. Acetic acid has a marked tendency, owing to the formation of soluble basic acetates, to retain the hydroxides in solution even though the pH's at which they are normally precipitated may have been exceeded (*vide* p. 160). These acetate solutions are, however, completely decomposed on boiling, although long boiling may be necessary if too much acetate has been used.

In the presence of an excess of phosphoric acid, ferric, aluminium and chromium phosphates can be precipitated completely at much lower pH values than are indicated in Fig. 138, especially if the solution is boiled. Under such conditions, ferric phosphate may be precipitated at pH 1·5, aluminium phosphate at pH 2·5 and chromium phosphate at pH 3·0. This is the principle underlying the separation processes of Smith (*J. Chem. Soc.*, 1933, 254) and Austin (*Analyst*, 1940, 65, 325), set out in Tables 189 and 190. Smith adds an excess of $(NH_4)_2HPO_4$ to a solution which is buffered at pH 3, whereas Austin uses the potassium salt and buffers the solution at pH 3·2-3·4. The amount of phosphate reagent used is designed to be rather more than is required to convert the three tervalent metals completely into insoluble phosphates, but any excess of alkali- or ammonium-phosphate left

in solution is prevented from causing the precipitation of any of the remaining metals as phosphates by the maintenance of relatively low pH values. Austin takes advantage of the fact that the sulphides of zinc, cobalt and nickel can be precipitated at pH 4·6–4·8 (see p. 138). If the pH is allowed to rise to higher values there is a risk of other phosphates being precipitated.

TABLE 189

SMITH'S SEPARATION IN PRESENCE OF PHOSPHATES

After removing Group I and II precipitates, boiling off H_2S, and boiling with a few drops of conc. HNO_3 and cooling, add NH_4Cl, NH_4OH and an excess of $(NH_4)_2HPO_4$, which precipitates the phosphates of the remaining metals, except Na, K and NH_4, which must be tested for individually. Test about one-tenth of the phosphate precipitate for Mn with HNO_3 and $NaBiO_3$. Dissolve remainder of precipitate in dilute HCl, dilute to 60–70 c.c., add NH_4OH to pH 3 (approx.), indicated by the orange-yellow of benzylaniline-azobenzene sulphonic acid (use 1 or 2 drops only). Then add 10–20 c.c. of pH 3 *formate buffer* (prepared by taking 57 grams of sodium formate, 85 c.c. of 23·5 N-formic acid and making up to 1 litre) ; boil and slowly add 10 c.c. of 8 N-$(NH_4)_2SO_4$. Filter.

Precipitate.		Filtrate.	
Phosphates of Al, Cr, Fe··· *Sulphates of Ba, Sr.* To precipitate add H_2O, Na_2SO_4 and Na_2O_2 ; boil, cool, filter.		Zn, Ca, Co, Ni, Mg, Mn. Heat ; pass H_2S ; filter.	
		Ppt. ZnS	*Filtrate.* Concentrate ; add $(NH_4)_2C_2O_4$; stand (5 minutes to 1–2 hours, if traces of Ca are sought).
Precipitate. Boil with dilute H_2SO_4, filter.	*Filtrate.* Test for Al and Cr.	*Ppt.* CaC_2O_4	*Filtrate.* Test separate portions for *Co* with α-nitroso-β-naphthol. *Ni* with dimethylglyoxime. *Mg* with Titan Yellow. (1) The possibility of interference from Co and Ni must be first removed by adding KCN, then HCl, and afterwards NaOH. Mg then gives Red precipitate with Titan Yellow. (2) If Mn is present in quantity, Mg must be separated by KCN and N4OH, before carrying out the test.
Residue. Test for Ba and Sr.	*Filtrate.* Test for Fe···		

TABLE 190
AUSTIN'S SEPARATION IN PRESENCE OF PHOSPHATES

Group I and II precipitates are removed, H_2S expelled from filtrate, any iron present oxidised, and the filtrate reduced to 20 c.c.

Add 2 N-NaOH drop by drop until slight precipitate persists for 20 seconds. Dissolve by adding 1 c.c. 5 N-HCl. Raise to boiling, add 2 c.c. 10 per cent. Na_2SO_4; if a precipitate is obtained add a further 2 c.c. of Na_2SO_4 and boil on water-bath for 15 minutes. Filter and wash precipitate with 0·05 $N-H_2SO_4$.

Ppt. $SrSO_4$ $BaSO_4$	*Filtrate.* Dilute to 100 c.c.; heat and add 3 c.c. of glacial acetic acid and 2 c.c. 3 M.-NaNO$_2$. Boil ½ minute. Add 0-4 c.c. M.-KH$_2$PO$_4$. Add 3 c.c. N-sodium acetate and then sufficient to reach pH 3·2–3·4 (spot test with bromophenol blue :—grey-green colour). Boil for 3 minutes. Filter, wash precipitate with hot 0·01 N-acetic acid.			
	Ppt. $FePO_4$ $AlPO_4$ $CrPO_4$	*Filtrate.* Boil; add 15 c.c. 3N sodium acetate to buffer solution at pH 4·6–4·8. Pass H$_2$S at 70°–80°. If no precipitate in 2 minutes, Zn, Co, Ni absent; otherwise pass H$_2$S for 5–10 minutes. Filter, wash precipitate with 0·1 N-HAc.		
		Ppt. ZnS CoS NiS	*Filtrate* (150–250 c.c.). Boil off H$_2$S. Add NaClO drop by drop. If no precipitate with 2 c.c., Mn absent, otherwise continue addition until precipitate darkens. Filter, wash precipitate with H$_2$O, then 0·1 N-HNO$_3$ and finally with H$_2$O.	
			Ppt. MnO_2	*Filtrate.* To hot solution, add 5 c.c. M.-citric acid + 20 c.c. saturated $(NH_4)_2C_2O_4$. Stand for 5 minutes. Filter, wash.
			Ppt. CaC_2O_4, H_2O	*Filtrate.* Test for Mg.

CHAPTER XXVIII

THE REACTION BETWEEN WEAK ORGANIC ACIDS AND INORGANIC BASES

In Chapter X it was shown that when a strong base has neutralised a weak monobasic acid or the final stage of a polybasic acid to the extent of 99 per cent., the pH then set up is equal to pK + 2, where K is the dissociation constant of the weak acid or else that of final stage of ionisation of a di- or tribasic acid. This principle, of course, applies only to the formation of salts which ionise in solution in a normal manner. Yet it is a common practice in organic chemistry to prepare the copper salts of weak acids, which can usually be crystallised from aqueous solution in well-defined crystals. The dissociation constant of acetic acid is $10^{-4.73}$, whence the pH corresponding with 99 per cent. neutralisation with a strong base is pH 6.73. On the other hand, copper hydroxide (as a basic salt) is precipitated from ordinary cupric salt solutions in the vicinity of pH 5. It would appear therefore that copper hydroxide is unable to combine with acetic acid to form a soluble copper acetate. Nevertheless, such a salt can be crystallised from aqueous solution, and can be dissolved to give quite a stable solution having a pH of 5.84 (0.01 M.), which is appreciably higher than that at which copper hydroxide is normally precipitated. This could only be possible if the 'copper-ion concentration of cupric acetate solution is materially smaller than that of, say, copper sulphate solution of the same concentration. It seems highly probable, therefore, that salts of weak metallic bases and weak acids must ionise abnormally, which ionisation is intimately connected with the fact that the salts must be appreciably hydrolysed in solution. This is the same as saying that in solution these salts must split up to give free acid and basic salts, which undergo some form of ionisation. It might be difficult to imagine basic salts remaining in solution, but it must not be forgotten that basic acetates of weak metallic bases such as those of lead, copper, aluminium, beryllium, thorium, zirconium and even ferric ion can be obtained which give apparently clear aqueous solutions, although it is very probable that their existence in solution is intrinsically colloidal. •

The Neutralisation of Acetic Acid with Typical Weak Metallic Bases.

Britton and Meek (*J. Chem. Soc.*, 1931, 2831) have measured the pH (with quinhydrone) during the progressive neutralisation of acetic acid with copper, lead, beryllium, aluminium and thorium hydroxides. The concentrations of the total acetic acid in the solutions were: 0·0197 N in the case of the lead solutions;
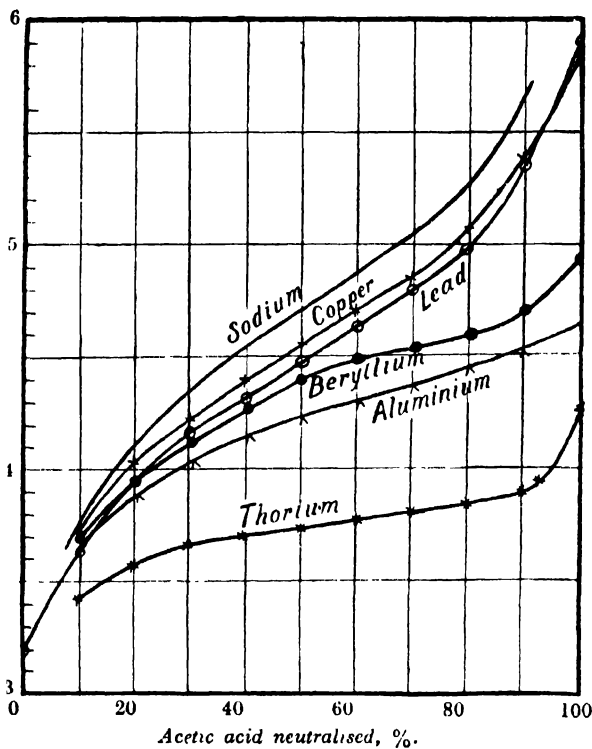
FIG. 139.—Neutralisation of Acetic Acid with Typical Inorganic Bases.

0·01965 N, copper; 0·0135 N, beryllium; 0·0213 N, aluminium; and 0·0170 N, thorium. Fig. 139 illustrates the change in pH, and also includes the curve corresponding to the pH values which would have been set up if sodium hydroxide had been used instead of the various weak metallic bases.

If the above metallic acetates were normal as regards their mode of ionisation, and also underwent ionisation to the same extent as does sodium acetate, then it would be expected that all

the curves given in Fig. 139 would be very similar and almost coincident. This is seen not to be the case. It is significant however, that, with the exception of beryllium, the acetates of those hydroxides having the highest precipitation pH values, *viz.*, copper and lead, lie nearest to the sodium curve. The pH at which copper ordinarily becomes precipitable as hydroxide is 5, whilst that for lead is approximately 6. Although beryllium hydroxide begins to precipitate at pH 5·7, the first equivalent of an acid which combines with the base does so in a remarkable manner (see p. 76) and it is evidently this characteristic of beryllium hydroxide that is reflected in the latter portion of the acetate curve in Fig. 140. The aluminium and thorium curves are still lower and lie in the order of the precipitation pH values of the respective hydroxides, *viz.*, 4·1 and 3·5.

The pH data permit of calculations of the ratio of the concentration of acetate ions to that of undissociated acetic acid of the various solutions. Such calculations were made on the basis of

$$pH = pK_{HAc} + \log \frac{[Ac']}{[HAc]},$$

and are summarised in Table 191.

<div align="center">

TABLE 191

RATIOS [Ac']/[HAc]

</div>

Neutralisation, per Cent.	Na.	Pb.	Cu.	Al.	Th.	Be.
10	0·10	0·08	0·10	0·08	0·05	0 09
20	0·23	0·16	0·20	0·14	0·07	0·16
30	0·39	0·26	0·31	0·20	0·09	0·25
40	0·63	0·36	0·45	0·26	0·09	0·34
50	0·91	0·55	0·66	0·32	0·10	0·46
60	1·35	0·81	0 91	0·35	0·11	0·56
70	2 09	1·15	1·29	0·44	0·12	0·63
80	3·63	1·74	2·24	0·55	0·13	0·72
90	8·13	4 17	4·47	0·62	0·14	0·91
100	100	14·45	12·88	0·81	0·38	1·32

Compared with the ratios corresponding to the sodium acetate-acetic acid mixtures, those of the aluminium, thorium, and beryllium acetates are all extremely low. Those of lead and copper, although much smaller, show relatively less deviation. The acetates of copper and lead, having hydroxide precipitation pH values which almost permit complete combination with acetic

acid, would be expected to approximate more closely to the ideal conditions represented by the sodium ratios.

Although solutions of these metal acetates have appreciable electrical conductivities, they áre much smaller than those of their respective salts with strong acids. In view of the foregoing observations it is not justifiable to assume that these conductivities merely indicate diminished ionisation, thus

$$PbAc_2 \rightleftharpoons Pb^{..} + 2Ac'$$
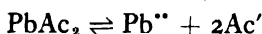
but are rather to be attributed to some such process as

$$PbAc_2 + xH_2O \rightleftharpoons Pb(OH)_xAc_{2-x} + xHAc,$$
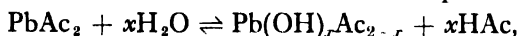
the basic acetate ionising in a complex manner ; very probably as a colloidal electrolyte.

Solutions of Basic Acetates.

It has long been known that soluble basic acetates of lead, copper, aluminium, beryllium, and thorium may exist in solution. As far back as 1854, Crum (*Annalen*, **89**, 156) obtained basic aluminium acetate, $Al(OH)(CH_3.CO_2)_2,1\cdot5H_2O$, which was readily soluble in water, and Berzelius (*Pogg. Ann.*, **2**, 242) found that a cold solution of copper acetate could be treated with much ammonium hydroxide before precipitation of a basic acetate began. Jackson (*J. Amer. Chem. Soc.*, 1914, **36**, 2347) isolated the basic lead acetates,

$$3Pb(CH_3.CO_2)_2,PbO,3H_2O \text{ and } Pb(CH_3.CO_2)_2,2PbO,4H_2O,$$

which were exceedingly soluble in water, whilst Langecker (*Biochem. Z.*, 1921, **122**, 34) obtained lead acetate solutions which dissolved as much as 3 molecules of lead oxide. Relatively little enquiry of a physicochemical character has been made into the nature of these basic solutions, though Parsons (*J. Physical Chem.*, 1907, **11**, 659) observed that the freezing-point of a lead acetate solution was raised somewhat on dissolution of lead hydroxide. From cryoscopic determinations, Blomberg (*Z. Elektrochem.*, 1915, **21**, 438) postulated that lead acetate ionises thus,

$$2PbAc_2 \rightleftharpoons PbAc^. + PbAc_3',$$

and also showed that the lead-ion concentration of a normal solution was exceedingly small.

Britton and Meek have investigated a number of solutions of basic lead acetate and their results are summarised in Table 192.

The lead-ion concentrations were measured potentiometrically, and the column headed *i* gives the percentages of lead in the solutions in the ionised state.

TABLE 192

Conc. of Pb.	Conc. of Soluble Basic Acetate, $Pb(Ac)_x(OH)_y$.		pH.	Spec. Cond. $\times 10^5$ mho.		[Pb⁗] $\times 10^6$.	i, per cent.	[Pb⁗][OH′]¹ $\times 10^{17}$.
	$x =$	$y =$		Basic.	Normal.			
0·715M.	1·974	0·026	6·13	8·69	8·78	4·79	0·67	0·05
0·728	1·814	0·186	6·38	8·39	8·82	2·95	0·41	0·09
0·428	1·068	0·932	7·60	6·25	7·62	0·28	0·07	2·34
0·574	1·046	0·954	7·38	7·28	8·27	0·68	0·12	2·04

The pH values of the basic lead acetate solutions are seen from Table 192 to increase as the acetate contents diminish and tend to exceed the pH value at which lead hydroxide is normally precipitated. As the pH values are determined by the ratio [Ac′] : [HAc], it follows that the higher pH values are to be attributed to a diminution in the concentrations of hydrolysed acetic acid, consequent upon the dissolution of further amounts of lead oxide. Table 192 reveals that the specific conductivities of the basic acetates are appreciably high in spite of the fact that the concentration of lead ions does not in any case exceed 1 per cent. of the total lead in solution. It also shows that the specific conductivity of a basic lead acetate solution is less than that of a normal lead acetate solution of the same lead concentration. Although the complex cation and anion theory of Blomberg might possibly explain the low lead-ion concentration of lead acetate solutions, it can scarcely be considered tenable in view of this evidence. The last column of Table 192 contains the products of lead- and hydroxyl-ion concentrations of the basic acetate solutions. Comparison with the solubility product of lead hydroxide given in Table 167 show that these products are of a similar magnitude, whence it follows that the solutions of basic lead acetate must have been on the point of precipitation.

Fig. 140 gives some precipitation curves with alkali from various metallic acetate solutions (Britton and Meek, *J. Chem. Soc.*, 1932, 183), together with curves referring to precipitation from strong acid salt solutions of the respective metals. Visible precipitation was delayed and coagulation occurred just before precipitation became complete, as indicated by the final inflexions. The beryllium reaction was an exception, for in this case precipitation began as soon as one equivalent of sodium hydroxide was added. The fact that higher pH values prevailed during the reactions is to be attributed to the reduced concentrations of the metallic ions and the buffer system existing between the hydrolysed acetic acid and the acetate ions.

If sodium acetate is added to solutions of acetates of weak metallic bases, the pH increases and exhibits buffer action between the hydrolysed acetic acid and the acetate ions. In this way, the normal precipitation pH values are appreciably exceeded without any precipitation occurring and there is no doubt that the solutions owe their stability to the excess of added sodium acetate. The simplest explanation is to assume the formation of complex ions. Thus Jaques (*Trans. Faraday Soc.*, 1910, 5, 225) attributed the
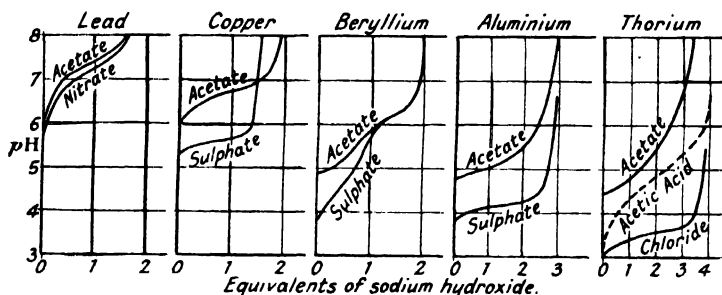
FIG. 140.—NaOH Precipitations from Metallic Acetate Solutions.

stability of sodium acetate–lead acetate solutions to the formation of complex acetate anions containing lead. If this were the case, it might be expected that the lead acetate in being incorporated in the complex anion would cease to be hydrolysed in the presence of a sufficient excess of sodium acetate. Britton and Meek, however, have shown that hydrolysis increases, showing that the basic lead acetate held in solution becomes increasingly basic, and incidentally that the concentration of lead ions undergoes a rapid decrease. This decrease in lead-ion concentration explains the solubility of lead sulphate in sodium acetate solutions.

The Neutralisation of Malonic Acid with Typical Metallic Bases.

Dibasic acids, such as oxalic and malonic, are characterised by their second stage of dissociation, being essentially that of comparatively weak acids. Thus at ordinary concentrations K_2 of oxalic acid is $1 \cdot 3 \times 10^{-4}$ whilst that of malonic is much smaller, $4 \cdot 4 \times 10^{-6}$. It would be expected, therefore, that many of the weaker metallic bases, *e.g.*, aluminium hydroxide, are unable to react with the hydrogen ions originating from their secondary ionisation, at any rate in a normal manner. On the contrary, what appear to be the normal oxalates and malonates of a few

weak bases can be isolated in a crystalline form, *e.g.*, those of zinc and copper, although this is not true of the very weak bases, *e.g.*, chromium, ferric and aluminium hydroxides. Nevertheless, well-defined complex oxalates and malonates of chromium, tervalent iron and aluminium can be prepared in conjunction with the appropriate sodium, potassium and ammonium salts. They have the general formulæ :

$$M_3[R(C_2O_4)_3] \text{ and } M_3[R(CH_2 < C_2O_4)_3],$$

where M is an alkali metal or ammonium and R, either $Fe^{...}$, $Cr^{...}$ or $Al^{...}$. It should be mentioned that both zinc and copper oxalates are sparingly soluble in water, but that they dissolve in sodium oxalate solutions, their solubility increasing with the concentration of sodium oxalate. The author (*J. Chem. Soc.*, 1926, 275) has advanced the view that these complex salts might owe their existence to the ability of the weak bases being able to react only with the first stage, being that of a relatively strong acid, of oxalic acid (similarly with malonic acid), whereas the strong bases, *e.g.*, NaOH and KOH, and even ammonium hydroxide are able to neutralise the second stage of ionisation.

For example :

$$Cr(OH)_3 + 3H_IH_{II}C_2O_4 \rightarrow Cr(H_{II}C_2O_4)_3 + 3H_2O$$
$$3KOH + Cr(H_{II}C_2O_4)_3 \rightarrow Cr(KC_2O_4)_3 + 3H_2O$$
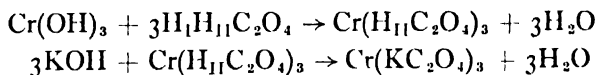
In a similar way the formation of sodium cupri-oxalate may be explained :

$$Cu(OH)_2 + 2H_IH_{II}C_2O_4 \rightarrow Cu(H_{II}C_2O_4)_2 + 2H_2O$$
$$2NaOH + Cu(H_{II}C_2O_4)_2 \rightarrow Cu(NaC_2O_4)_2 + 2H_2O.$$
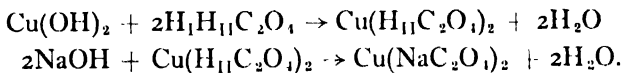
H_I refers to the hydrogen ion originating from the first stage of ionisation, and H_{II} to the hydrogen ion from the second.

Britton and Jarrett (*J. Chem. Soc.*, 1936, 1489) have investigated the formation of $Na_2Cu(C_2O_4)_2$ electrometrically and by means of the phase rule and concluded that the complex salt ionises to give the complex anion, $Cu(C_2O_4)_2''$. They have also studied the complex malonates of chromium, aluminium and tervalent iron (*J. Chem. Soc.*, 1935, 1728) and the corresponding complex oxalates (*vide* Jarrett, Ph.D. Thesis, London, 1935), which work included an investigation of the possible stereoisomerism, which Werner (*Ber.*, 1912, **45**, 865) claimed to exist.

Fig. 141 illustrates the change in specific conductivity and pH when 0·04 M. malonic acid is progressively neutralised with sodium, magnesium and zinc hydroxides (curves marked A) and when 0·02 M. malonic acid is treated with increasing amounts of

chromium, aluminium, beryllium and copper hydroxides (curves marked B).

Knowing that pK_2 of malonic acid is 5·36, it follows that neutralisation from 1 per cent. to 99 per cent. of the hydromalonate ion occurs between pH 3·36 and 7·36. As magnesium hydroxide is not precipitated until pH 10·5, it might have been
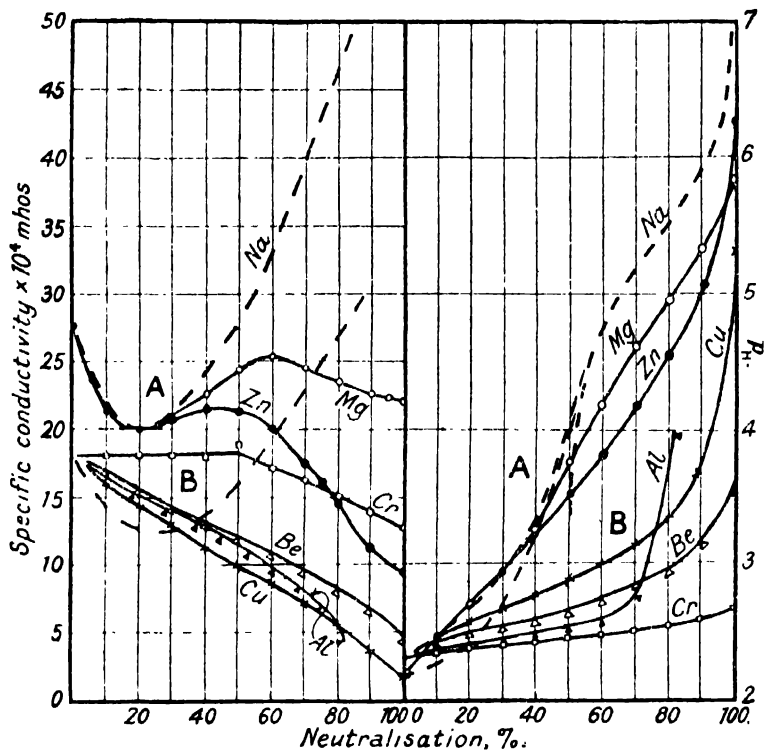
FIG. 141.—Neutralisation of Malonic Acid with Typical Inorganic Bases.

considered that this base would combine in a normal way with both stages of malonic acid. Reasoning along these lines, zinc hydroxide would appear to be incapable of complete neutralisation, whilst the bases that suffer precipitation within the range pH 4–6 could not be expected to react with little more than the first stage. Fig. 141 shows this to be the case.

The conductivity curves (A) corresponding to the two stronger bases, magnesium and zinc hydroxides, show, as do also the pH curves, that the reaction of malonic acid with the first 0·5 equivalent of base tends to be normal, in that the curves

almost coincide with the sodium curve, the variations in specific conductivity introduced by the different mobilities of the cations being negligible at such dilutions. This shows that the bases are able to combine with the first stage to form magnesium and zinc hydrogen malonates, which ionise to an extent similar to sodium hydrogen malonate at the same dilution. Between 25 and 50–60 per cent. neutralisation, the conductivities fall below that of the sodium salt and, after attaining maxima, decrease as more magnesium and zinc malonate are formed. The fact that zinc hydroxide is a weaker base than magnesium hydroxide is apparent from the greater diminution in conductivity in the case of zinc. Except for the pH values of magnesium and zinc malonate solutions, *i.e.*, at 100 per cent. neutralisation, the weakness of magnesium and zinc hydroxides compared with that of sodium seems also to be reflected in the relative positions of the pH curves between 50 and 100 per cent. neutralisation, the zinc curve again lying below that of magnesium. As the pH values result from the equilibium $HM' \rightleftharpoons H^{\cdot} + M''$, it follows that the lower pH values represented by the zinc and magnesium curves indicate much lower ratios of malonate to hydrogen malonate ions. This must be attributed chiefly to diminished concentrations of malonate ions which originate from the substances formed by the reaction of the zinc and magnesium hydrogen malonates with further amounts of the respective base. The effect of the much weaker second stage is thus made apparent.

The conductivity and pH curves (B) of the series of the yet weaker bases, when compared with the appropriate sodium curves, show that the equilibrium $H_2M \rightleftharpoons HM' + H^{\cdot}$ is now the controlling factor.

Double Decomposition Reactions between Heavy-metal Salts and Sodium Malonate.

The reactions occurring during the progressive addition of sodium malonate to dilute solutions of either the chloride or the sulphate of various metals were studied by Britton and Jarrett (*J. Chem. Soc.*, 1935, 1728) with the glass electrode. If simple double decomposition takes place, immediately the stoicheiometric amounts of alkali malonate are added the pH values of the solutions should rise to values corresponding to the presence of free sodium malonate, *viz.*, to

$$p\text{H} = \tfrac{1}{2}(p\text{K}_2 + p\text{K}_{w} + \log c) = 9\cdot78 + \tfrac{1}{2}\log c,$$

where c is the concentration of the excess of added sodium malonate. Fig. 142 gives the variations in pH which occur on

adding 0·1 M.-sodium malonate to 100 c.c. of each of the solutions : 0·02 M.-FeCl₃, 0·02 M.-CrCl₃, 0·01 M.-Al₂(SO₄)₄ ; and 0·05 M.-sodium malonate to 100 c.c. of each of the solutions : 0·02 M.-CuSO₄, 0·02 M.-BeSO₄ and 0·02 M.-UO₂Cl₂ ; 0·02 M.-MgSO₄ and 0·02 M.-zinc sulphate.

Excepting the curves of magnesium, zinc and chromium, the curves are inflected at a point·corresponding with slightly more
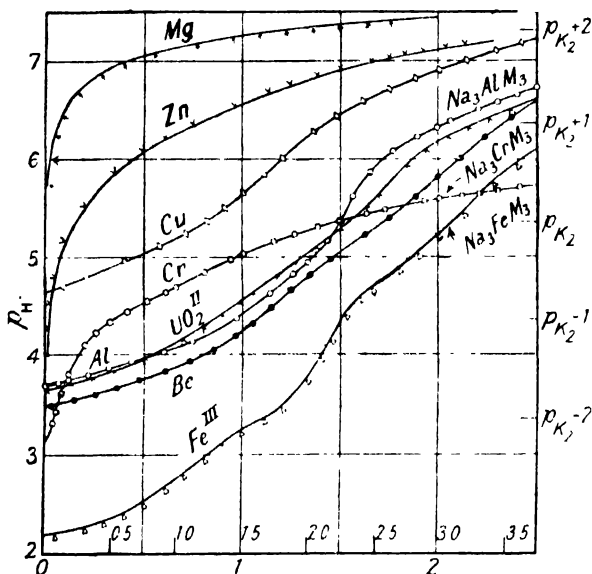
Fig. 142.—pH changes produced during the addition of Sodium Malonate to Metallic Salt Solutions.

Sodium Malonate, Mols : Upper Scale—Al,Cr,Fe···
Lower Scale—Mg,Zn,Cu,UO₂Be.

than the stoicheiometrical amount of sodium malonate. Comparison of the pH values thereafter set up with pH $= p$K₂ of malonic acid, given at the right of Fig. 142, shows that some of the hydrogen ions of the second·stage of ionisation of malonic acid could not possibly have reacted with the heavy metal bases involved. The curves of the two strongest bases, *viz.*, magnesium and zinc, indicate pH values in the region of pK₂ $+$ 2, whence it follows that the concentrations of hydromalonate ions were exceedingly small. The pH values, and the potentials of the appropriate metal electrodes, indicate that the zinc and copper

solutions to which excess of alkali malonate had been added were on the verge of precipitating the hydroxides.

The failure of sodium malonate to precipitate a heavy metal base, even though the pH at which the base is ordinarily precipitated may be exceeded, as in the ferric, aluminium and copper salt titrations, may be due to the retention of the hydroxide in solution as a basic hydromalonate, stabilised in some way by the alkali malonate, or else to the formation of complex anions. If the latter were formed completely, then no hydromalonate ions should be present in the solutions, but the pH values obtained during the titrations involving the weaker bases certainly show their presence. As greater excesses of sodium malonate are added, relatively high pII values are established, which indicate the gradual disappearance of such ions. Britton and Jarrett show that under these conditions there is reason to believe that complex anions are formed, and this is especially true of copper, when the complex salt Na_2CuMal_2 is formed, yielding the complex anion, $CuMal_2''$.

On the other hand, these authors investigated the change in pH when malonic acid solutions of magnesium, zinc, copper, ferric, beryllium, chromium and aluminium hydroxides were neutralised with alkali, in order to see whether there was any possibility of the respective complex malonic acids, $e.g.$, H_2CuMal_2, H_3AlMal_3, H_3FeMal_3, existing in the dissolved state.

Whilst no evidence of these complex acids was forthcoming, it was found that the heavy metals were held in solution as very feebly ionised hydromalonates. Precipitation with alkali from these solutions was considerably delayed. Thus zinc precipitation occurred at about pII 8 instead of at pH 7 ; copper between pII 6·1 and 8·3, depending on the relative amounts of copper hydroxide and malonic acid originally in the solution, instead of pH 5·4 ; ferric hydroxide, pH 6·5- 8·0 instead of pII 2 ; beryllium hydroxide, pII 6·6–8·2 instead of pH 5·7 ; aluminium hydroxide, pH 7·5–8·0 instead of pII 4·1. Chromium hydroxide failed to be precipitated with alkali.

The pH values set up in the aluminium and ferric titrations at the points when the complex salts, Na_3AlMal_3 and Na_3FeMal_3, should have been formed compared well with those of solutions of these salts, previously prepared in the crystalline form. Alkali chromimalonates gave solutions of appreciably higher pII values than those prepared in solution and the complex is very much more resistant to attack by alkali as shown by the higher pII values produced when treated with alkali.

Complex Formation involving Metallic Acids and Bases and Hydroxy Acids.

In analytical chemistry, use is sometimes made of the fact that certain metallic bases can be maintained in alkaline solution if a hydroxy acid, such as tartaric or citric, is added prior to the addition of the alkali. An excellent example of such a solution is Fehling's solution, in which a tartrate in the form of Rochelle salt is added to copper sulphate in order to prevent the precipitation of copper hydroxide with the sodium hydroxide. The complex formation which occurs between copper sulphate and alkali tartrate has received most attention and, probably owing to the intense blue colour of the solution, and to the fact that when the solution is electrolysed the blue colour migrates towards the anode, it has been tacitly assumed that a complex cupri-tartrate anion exists. Copper tartrate on treatment with alkali is gradually decomposed, and when sufficient has been added to convert it into the basic tartrate, represented by $Cu(OH)_{1.25}T_{0.38}$, it dissolves and almost immediately the solution becomes alkaline. In alkaline solution, however, the basic copper tartrate becomes slightly more basic. The retention of the basic tartrate is intimately linked with the tartrate ions in solution and there is no doubt that the hydroxy groups contribute to the stability of the complex basic tartrate solutions. It is, of course, quite possible that the weakness of the hydroxy acids is also conducive to complex formation, as is the case with acetic, malonic and oxalic acids, but, in general, the hydroxy acid complexes are much more stable. Hydroxy compounds, which contain no acid groups, e.g., glycerol and dextrose, can prevent precipitation if added to salt solutions before treating with alkali. Thus dextrose in zirconium chloride solution prevents the precipitation of zirconia with alkali, although Britton (J. Chem. Soc., 1926, 269) has shown by means of the hydrogen electrode that the zirconium chloride is converted quantitatively into zirconium hydroxide. Similarly, glycerol will prevent the precipitation of ferric hydroxide from a ferric salt solution.

It is not possible to say whether the metallic bases do actually unite with the hydroxy groups. Glycerol and the hydroxy groups of phenol and salicylic acid are feebly acidic, yet their dissociation constants can be measured. If the hydroxy groups of tartaric, malic and citric acids are acidic, then their ionisation must be so extremely slight that their respective dissociation constants cannot be measured by electrometric methods. Menzies (J. Chem. Soc., 1925, **127**, 2369) prepared tetrathallium tartrate

in which both hydroxy groups are combined with thallous hydroxide. It may be that such a salt owes its existence to its sparing solubility in water, for no salts of either lactic, malic, tartaric or citric acids have been prepared with sodium and potassium hydroxides in which the hydroxy groups have been involved. Moreover, complex formation with hydroxy acids occurs not only with basic oxides but also with acidic oxides such as boric acid, arsenious oxide, molybdic and tungstic acids. As may be inferred from the foregoing argument there may be some grounds for believing that the hydroxy groups might possibly behave as exceedingly weak acids and therefore react with bases, but there are absolutely no grounds for the view that they might also function as exceedingly weak bases and so react with acids. Owing to the extreme weakness of the hydroxy group, either as an acid, or conceivably as a base, any products of such a reaction would be insoluble in water, otherwise they would undergo complete hydrolysis. Although their insolubility does not necessarily mean that they would separate as precipitates, for they may constitute a highly dispersed phase. As the complex solutions are usually clear it would be necessary to assume that the complexes are composed of relatively large aggregates, which, however, are not of sufficient magnitude to give the Tyndall Beam. Another possibility is that the combination occurs by means of co-valent linkages.

showed that it was possible to investigate the formation and constitution of these complex tartrate solutions by means of pH electrometric titration and during the last ten years electrometric, optical and other physico-chemical methods have been applied by his students, W. E. Battrick, K. O. P. Jackson, J. W. Dorling, A. A. Moss and H. A. Edge, and their work is described in the respective Ph.D. theses (London, 1933, 1934, 1936, 1937, 1938).

Morton (*Quart. J. Pharm.*, 1930, **3**, 561) has investigated, by means of the glass electrode, the complexes formed when solutions of bismuth salts and either citric acid or sodium citrate is subjected to the action of sodium hydroxide. In so doing, the bismuth passes into solution which is not precipitated by adding an excess of alkali. He has shown that these solutions contain a basic bismuth citrate complex.

Boric Acid Complex Formation.

Biot observed in 1835 that boric acid increased the rotatory power of tartaric acid solutions. It also increases the electrical conductivity (Magnanini, *Gazzetta*, 1891, **21**, (ii), 215 ; Amadori,

ibid., 1931, **61**, (ii), 215) and the hydrogen-ion concentration (Rimbach and Ley, *Z. physikal. Chem.*, 1922, **100**, 393 ; Burgess and Hunter, *J. Chem. Soc.*, 1929, 2838). These properties are usually ascribed to the formation of a complex borotartaric acid, and such a view seems admissible from the fact that boric acid diminishes the conductivity of solutions of sodium tartrate (Magnanini and Bentivoglio, *Gazzetta*, 1893, **23**, (ii), 451) apparently owing to the formation of a borotartrate ion having a lower mobility than that of the tartrate.

Potentiometric titrations of solutions of mixtures of boric and tartaric acids have been described by Burgess and Hunter, Lowry (*J. Chem. Soc.*, 1929, 2853), and by Britton and Jackson (*ibid.*, 1934, 1002), which indicate that boric acid has a pronounced effect in strengthening the tartaric acid in its initial stage of neutralisation and weakening it somewhat in the final. The first authors considered their curve to point to the dibasicity of borotartaric acid, whilst Lowry suggested that the final weakness might be caused by " a little extra work to detach the last carboxyl from the boron."

Many attempts have been made to isolate the complex acid salts in crystalline form from solution, and numerous substances have been described. Burgess and Hunter determined the isotherms at 0°, 25°, and 50° of the ternary system boric acid–tartaric acid–water, but found no evidence of any solid complex acid, the only solid phases being the two simple acids (see also Bancroft and Davis, *J. Physical Chem.*, 1930, **34**, 2479). Lowry, and Bancroft and Davis have isolated a potassium borotartrate, $KB(C_4H_4O_6)_2$, in which the boron is believed to be present as the result of a quadricovalent linkage. The ammonium salt and the analogous potassium boromalate have since been described by Jones (*J. Chem. Soc.*, 1933, 951). The existence of such a salt in solution, however, is not substantiated by pH neutralisation curves. Fig. 143 illustrates the effect which boric acid has on tartaric acid. The heavy curve at the bottom of Fig. 143 is that of the titration of 50 c.c. of 0·1 M.-tartaric acid with 0·2771 M.-sodium hydroxide at 18° and was obtained by means of the hydrogen electrode. The thinner lines, taken in order downwards, refer to the titration of mixtures of 0·1 M.-tartaric acid with 0·05 M., 0·075 M., 0·3161 M., and 0·5 M.-boric acid respectively. Even in such dilute solutions, the boric acid is thus seen to have a marked effect in increasing the strength of the acid, the precise amount depending upon the proportion of boric acid to tartaric acid in the solution. The borotartaric acid curves either cross, or tend to cross, the tartaric acid curve at a point

corresponding approximately to three-quarters neutralisation of the tartaric acid.   Immediately after the addition of 2 equivalents of alkali, the curves exactly follow the course of neutralisation of boric acid, and in every case the pH value at the mid-point of these sections is equal to $p\mathrm{K}_{\mathrm{HBO_2}}$.   The intersection of the borotartaric acid curves with those of tartaric acid at about three-fourths neutralisation is more apparent in the middle and upper
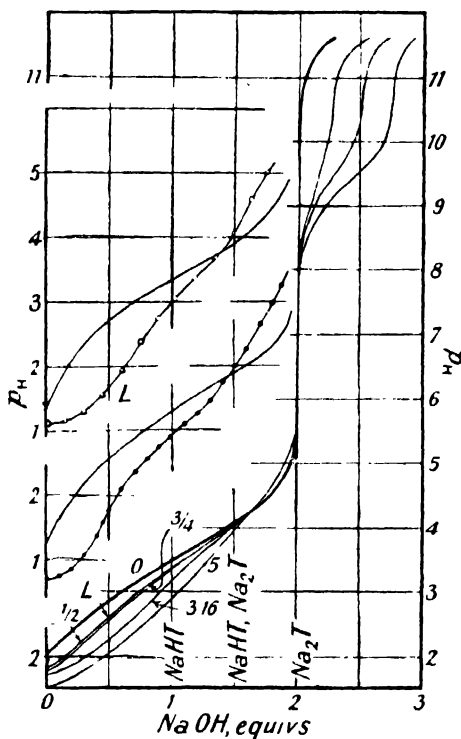
Fig. 143. —pH Neutralisation Curves of Tartaric Acid in the presence of Various Amounts of Boric Acid.
(Britton and Jackson, *J. Chem. Soc.*, 1934, 1002.)

pairs of curves (set out separately).   They correspond respectively to the titrations of 50 c.c. of 1 M.-tartaric acid, and of 1 M.-tartaric acid + 0·5 M.-boric acid, with 2 M.-sodium hydroxide ;   and 50 c.c. of 0·5 M.-tartaric acid, and of 0·5 M.-tartaric acid + 0·5 M.-boric acid, with 1·231 M.-sodium hydroxide.   These two pairs of curves are very similar to those described by Lowry for a 2 M.-tartaric acid + 1 M.-boric acid mixture.   The points marked

L indicate the pH values of solutions, the solutes of which are in the ratio required by Lowry's salt.

The fact that the curves intersect when the tartaric acid is three-quarters neutralised is something more than a coincidence, for Britton and Jackson showed that at this stage the optical activity reached a maximum value during each separate neutralisation. The precise value of the maximum depended on the relative amount of boric acid to tartaric acid, a large amount of boric acid resulting in a considerably enhanced optical activity.

It is exceedingly difficult to interpret these remarkable results, though it is possible that if a complex borotartaric acid does, indeed, exist, one of its salts is formed with $1 \cdot 5$ equivalents of alkali per molecule of tartaric acid and x molecules of boric acid.

Another feature of the boric acid problem is the effect, made use of on page 199 which polyalcohols, *e.g.*, glycerol and mannitol, have in increasing the dissociating power of boric acid, so much so that it can be titrated with alkali using phenolphthalein. Krantz, Carr and Beck (*J. Physical Chem.*, 1936, **40**, 927) observed that ethylene glycol, propylene glycol and their respective oxides are without effect, whereas the polyalcohols, erythriotol, pentærythritol, adonitol produced increases comparable with that given by mannitol. It is significant that glyceric aldehyde and dihydroxy acetone also compare with the action of mannitol. Erythritan has an even greater effect (see however, Böeseken, *Rec. trav. chim.*, 1921, **40**, 553). The effects produced by many other sugar alcohols on the dissociation of boric acid were also studied (Krantz, Oakley and Carr, *ibid.*, 1936, **40**, 151 ; Bell, Carr, Evans and Krantz, *ibid.*, 1938, **42**, 507).

Arsenious Acid Complex Formation.

Arsenious acid behaves as an extremely weak monobasic acid, $K = 5 \cdot 5 \times 10^{-10}$ (Britton and Jackson, *J. Chem. Soc.*, 1934, 1048). When mixed with tartaric acid and neutralised with alkali the optical activity is enhanced in a remarkable manner. The precise increases depend on the molecular ratio of the arsenious acid to tartaric acid, but as a rule maximum rotations for each ratio are obtained when the tartaric acid is half-neutralised. Some type of complex formation between the two acids undoubtedly takes place, and as Britton and Jackson have shown, some indication of it is also to be obtained from the pH neutralisation curves.

Owing to the extreme weakness of arsenious acid its ionisation in aqueous solution is so very small that it could not affect the ionisation of a moderately strong acid such as tartaric, if no inter-

action, of course, occurred.   Fig. 144 shows, however, that the
hydrogen-ion concentration of tartaric acid solutions is slightly
increased by the inclusion of arsenious oxide, and the enhanced
primary ionisation is reflected in the pH curves during neutralisa-
tion with one equivalent of alkali, being below that of tartaric acid
when alone.   The fact that during neutralisation with the second
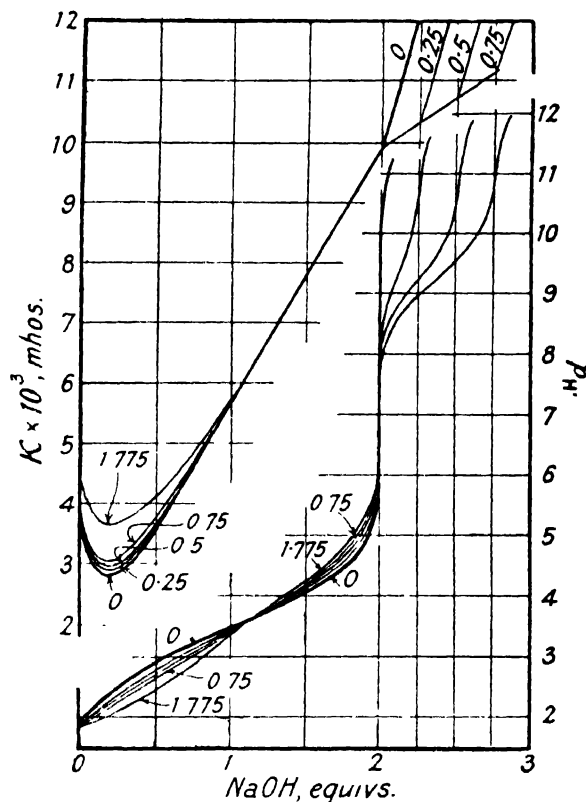
FIG. 144.—pH and Conductometric Curves of the Neutralisation of Tartaric
Acid in the Presence of Arsenious Acid.

equivalent of sodium hydroxide, i.e., with the amount necessary
to form sodium tartrate, the pH curves are higher than those
indicated by the tartaric acid curve, reveal that some kind of
combination must take place with the tartaric acid to reduce
its second dissociation constant.   The final stages of the titration
curves are merely those of the arsenious acid present to form
NaH_2AsO_3, or perhaps $NaAsO_2$.

The curves, which were obtained with the glass electrode, refer to the neutralisation of 75 c.c. of 0·1 M.-tartaric acid + x M.-arsenious acid solutions with 0·2771 N.-sodium hydroxide at 25° ; x being 0·025, 0·05, 0·075 and 0·1775. The numbers on the curves in Fig. 144 represent the molecular ratios of arsenious acid : tartaric acid. The curves, given in the upper section of Fig. 144, show the changes in specific conductivity which occurred during the respective neutralisation. The curves suggest that the complex formation does not exist in alkaline solution and this is borne out by the optical activity returning to that which would be expected from sodium tartrate alone.

Antimonous Oxide Complex Formation.

In a similar manner, antimonious oxide dissolves in tartaric acid and in so doing increases the first stage of ionisation but considerably reduces the second stage. Fig. 145 illustrates glass electrode titrations (Britton and Jackson, *J. Chem. Soc.*, 1934, 1055) of 50 c.c. of 0·1 M.-sodium emetic (*i.e.*, 0·1 M.-sodium bitartrate + 0·05 M.-Sb$_2$O$_3$) with 0·2 N-NaOH (curve marked Na Emetic); 50 c.c. of 0·1 M-sodium bitartrate + 0·025 M.-Sb$_2$O$_3$ (curve marked 0·5 Sb) with 0·2 M.-NaOH ; 50 c.c. of 0·1 M. sodium emetic with 0·1 M.-Na$_2$CO and also with 0·2 M.-NaHCO$_3$, the curves being correspondingly marked. The curve, NaHT, represents the neutralisation of 50 c.c. of 0·1 M.-sodium bitartrate with 0·2 M.-NaOH. Comparison of the "Na Emetic" and "0·5 Sb" curves with this curve reveals the considerable effect which the antimonious oxide has in diminishing the second stage of dissociation of tartaric acid. The arrows denote the incidence

FIG. 145.—Glass Electrode Curves of Solutions of Sb$_2$O$_3$ in Sodium Bitartrate.

of the precipitation of antimonious oxide. It will be seen that, whilst in the " 0·5 Sb " solution precipitation was delayed until pH 11 when the tartaric acid was completely neutralised, precipitation began at pH 7·5 from the emetic solution before the acid had been neutralised. Fig. 145 also explains why greater amounts of sodium bicarbonate and sodium carbonate are necessary to cause precipitation from emetic solutions, the main factor being the attainment of pH 7·5–7·6. These precipitates dissolve as more alkali is added, but it should be noted that considerably less alkali is needed for dissolution than is the case when alkali tartrate is absent from the solution. The optical rotation data show that some kind of complex formation between the antimonious oxide and sodium tartrate persists in alkaline solution, so much so that pronounced lævo-rotations may be established.

Molybdic and Tungstic Acid Complex Formation.

An interesting method of demonstrating the existence of complex formation between molybdic or tungstic acid and an organic acid is illustrated in Fig. 146 and taken from a paper
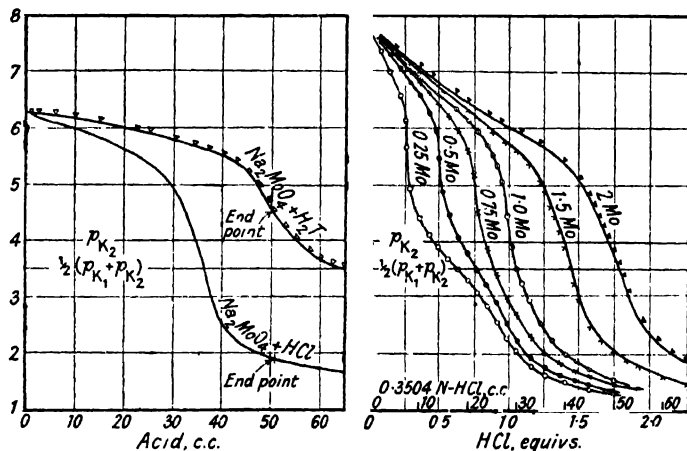
FIG. 146.—Quinhydrone Titration Curves showing Complex Formation between Sodium Tartrate and Molybdic Acid.

by Britton and Jackson (*J. Chem. Soc.*, 1934, 1055). This particular set of curves refer to quinhydrone electro-titrations of 50 c.c. of solutions that were each 0·1 M. with respect to sodium tartrate and successively 0·025, 0·05, 0·075, 0·10, 0·15 and 0·2 M. with respect to sodium molybdate.

The curves in Fig. 146 are inflected in the 0·25, 0·5, 0·75 and 1 titrations (these quantities are marked on the curves and refer to the molecular ratios of molybdate to tartrate in the solutions) when the added hydrochloric acid is exactly that required to react with the sodium molybdate to release molybdic oxide, MoO_3. This oxide must therefore combine with the sodium tartrate to form a complex salt, $Na_2(MoO_3)T$. It is significant that in the 1·5 and 2 titrations the inflexions appear some time before the amounts of hydrochloric acid required to liberate MoO_3 have been added, showing that in these circumstances some molybdic acid is not incorporated in the complex molybdo-tartrate.

That the complex salt is actually $Na_2(MoO_3)T$ can be confirmed by reading off from the curves the volume of hydrochloric acid which must be added to bring the pH to some desired value. Convenient pH values are those set up when (i) $pH = pK_2 = 4$, *i.e.*, corresponding to the buffer system given by equimolar amounts of sodium tartrate and sodium bitartrate,

and (ii) pH $\dfrac{pK_2 + pK_1}{2} = 3·5$,

i.e., corresponding to sodium bitartrate only. If the complex molybdi-tartrate contains the molybdic oxide together with an equimolar amount of tartrate in the complex ion, then such an ion would not be involved in the buffer systems produced on adding hydrochloric acid, and calculations based on the above principle show this to be the case.

This method was also employed by Britton and Jackson to prove the existence of sodium tungsti-tartrate ($Na_2(WO_3)T$), and Jarrett (Ph.D. Thesis, 1935, London) has found it applicable to the study of molybdi-oxalate and tungsti-oxalate complexes.

Basic Oxide Complex Formation.

The composition of various basic tartrate complexes, which are formed at the point when the solutions have reached pH 10, is shown in Table 193.

TABLE 193

COMPOSITION OF SOLUBLE BASIC TARTRATE
Complexes at pH10

Thorium	$Th(OH)_{3·00} T_{0·5}$
Bismuth	$Bi(OH)_{2·67} T_{0·17}$
Ferric	$Fe(OH)_{2·66} T_{0·17}$
Lanthanum	$La(OH)_{1·5} T_{0·75}$
Copper	$Cu(OH)_{1·39} T_{0·30}$
Cobalt	$Co(OH)_{1·13} T_{0·43}$
Nickel	$Ni(OH)_{1·62} T_{0·19}$

As the solutions are rendered more alkaline the complexes gradually become more basic. Thus Britton and Battrick (*J. Chem. Soc.*, 1932, 196) have shown that lanthanum tartrate passes into solution when it has become decomposed to the extent shown by $La(OH)_{1.40}T_{0.8}$, whilst in the presence of an excess of sodium hydroxide it corresponds with $La(OH)_{2.13}T_{0.44}$.

The stability of the basic tartrate complex in alkaline solutions depends both on the particular hydroxy acid involved and the metallic oxide. It seems to be a characteristic property of the metallic base rather than one of its strength as a base. Thus thorium hydroxide is a comparatively weak base whilst lanthanum hydroxide is moderately strong. Copper hydroxide is also a weak base. The tartrate complexes in the case of each of the bases are quite stable in the presence of an excess of alkali. On the other hand, manganous and ferric basic tartrate complexes are formed from a fairly strong and a very weak base respectively, yet they are decomposed in sufficiently alkaline solutions and the bases are precipitated. The composition of the basic tartrates in alkaline solution also depends on the physical treatment which has been accorded to the solutions—the metallic tartrates becoming more basic. With certain bases, such as that of tervalent iron, boiling converts the basic tartrate into ferric hydroxide which eventually is precipitated.

The nature of the hydroxy acid has a profound effect on the stability of the complex alkaline solutions. The order of the stability of the complex solutions produced by the various acids is

$$\text{citric} = \text{tartaric} > \text{malic} > \text{lactic} > \text{salicylic.}$$

The number of hydroxy groups in the acid molecule seems to have little effect in view of the fact that the citrate and tartrate complexes are of comparable stability. A factor of prime importance appears to be the magnitude of the dissociation constants of the hydroxy acids, particularly those corresponding to the first stage of ionisation. Thus the above order is approximately that of their respective primary constants.

A typical example of the use of pH titration curves in investigating the formation of complex tartrate solutions is illustrated in Fig. 147 (Britton and Battrick, *J. Chem. Soc.*, 1933, 5).

The variations in pH at 18°, measured by means of the hydrogen and quinhydrone electrodes, during the progressive addition of 0.05 M.-$Na_2C_4H_4O_6$ to 100 c.c. of 0.01 M.-$ThCl_4$ are indicated by curve I in Fig. 147. During the addition of the first 2.3 equivalents the pH fell to the low value of 2.07. At this point of maximum acidity, precipitation of basic thorium tartrate

began, but the precipitate had largely redissolved when 4 equivalents of tartrate had been added; the precise point at which complete dissolution took place depended on such factors as the rate of addition, agitation, and temperature. The pH curve corresponding to the addition of excess $Na_2C_4H_4O_6$ shows that the solution was strongly buffered in the region of pH 4 through the presence of the acid which had been liberated during precipitation and had failed to recombine with the Th on the dissolution of the basic tartrate.
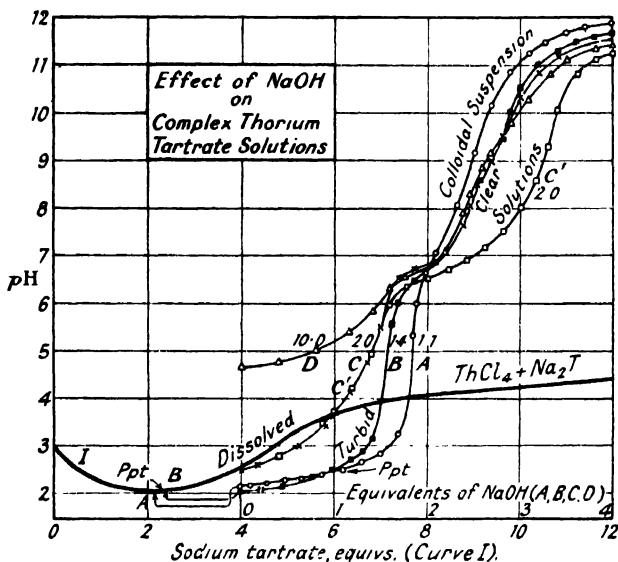
FIG. 147.—Curves illustrating the Formation of Complex Alkaline Tartrate Solutions of Basic Thorium Tartrate.

A series of hydrogen-electrode titrations with 0·1 N-NaOH was made on $ThCl_4$ solutions to which various proportions of $Na_2C_4H_4O_6$ had been added, viz., 1·1, 1·4, 2·0, and 10 molecules to 1 molecule $ThCl_4$. The respective curves are given in Fig. 147 and are marked A, B, C, and D. The solutions titrated were, respectively, 100 c.c. of 0·01 M.-$ThCl_4$ + 22·0 c.c. of 0·05 M.-$Na_2C_4H_4O_6$; 100 c.c. of 0·01 M.-$ThCl_4$ + 28 c.c. of 0·05 M.-$Na_2C_4H_4O_6$; 100 c.c. of 0·01 M.-$ThCl_4$ + 40 c.c. of 0·05 M.-$Na_2C_4H_4O_6$; and 100 c.c. of 0·01 M.-$ThCl_4$ + 40 c.c. of 0·25 M.-$Na_2C_4H_4O_6$. In the first case, the initially clear solution began to precipitate soon after 1 equivalent of NaOH had been added. Above pH 7 the precipitate passed into a fine

colloidal suspension, but at no time did the solution become entirely clear. In the other titrations, in which larger amounts of sodium tartrate were present, perfectly clear solutions were obtained. The initial sections of curves A, B, C and D refer to the neutralisation of the acid liberated in consequence of the initial precipitation of a basic tartrate when the sodium tartrate was added to the thorium chloride. The second sections, beginning at pH 6·5, refer to the partial decomposition of the basic tartrate which was accompanied by its dissolution as the result of complex formation.

Ageing the complex solutions, however, causes the basic tartrates to suffer more decomposition. Curve C′, which refers to the solutions employed in the titration which gave curve C, was constructed from the pH values of solutions to which various quantities of alkali had been added and which were then placed in stoppered bottles for several weeks, until repeated pH measurements showed that no further decomposition was occurring.

Further decomposition of the basic complexes also takes place in the presence of excess of alkali, as may be shown by backtitrations with hydrochloric acid.

Although a certain relative proportion of sodium tartrate must be present in the alkaline solution to stabilise the complex solution, there appears to be no simple stoicheiometric ratio between the alkali tartrate and the heavy metal in the soluble basic tartrate. In the case of thorium, 1·1–1·4 molecules of Na_2T appear to be the minimum amount just to maintain the basic thorium tartrate, $Th(OH)_xT_{2-x/2}$, in solution, where x, depending on conditions, may have any value ranging from 3·0 to 3·8.

CHAPTER XXIX

THE HYDROGEN-ION CONCENTRATION OF SOLUTIONS CONTAINING COMPLEX IONS

Complex Metal Cyanides

THE existence of complex cyanides in solution has been demonstrated by electrical migration experiments, conductivity and, in certain cases, by means of electromotive force measurements using the respective metal electrodes. Migration work has shown that the heavy metal is present in the complex anion (see Hittorf, *Pogg. Ann.*, 1853, **89**, 177; 1856, **98**, 1; Rieger, *Z. Elektrochem.*, 1901, **7**, 871), but investigation of the equivalent conductivities of solutions of complex cyanides has not always led to a definite confirmation of their supposed constitution. For instance, Walden (*Z. anorg. Chem.*, 1900, **23**, 373) found at 25° that Λ_{1024}—Λ_{32} for $K_2Zn(CN)_4$ and $K_2Cd(CN)_4$ was 14·9 and 15·1 respectively, neither of these values being sufficiently near 20 to indicate the dibasicity of the respective anions.

From E.M.F. measurements of cells involving amalgamated zinc and cadmium electrodes, Euler (*Ber.*, 1903, **36**, 3400) deduced the existence of $Zn(CN)_4''$ and $Cd(CN)_4''$, though Kunschert (*Z. anorg. Chem.*, 1904, **41**, 337), in order to account for the potentials of silver electrodes in solutions containing both silver and zinc complex cyanides, found it necessary to postulate the existence of another zinc complex ·cyanide ion, *viz.*, $Zn(CN)_3'$. This assumption, however, was based on the belief that the silver was contained in the complex anion, $Ag(CN)_2'$, which, according to Bodländer and Eberlein (*ibid.*, 1904, **39**, 197), is not strictly true, for they claim the co-existence of yet another anion, $Ag(CN)_3''$, in all except very dilute solutions.

Electrometric titrations by Britton and Dodd (*J. Chem. Soc.*, 1932, 1940) using metallic electrodes have also been useful in demonstrating the formation of $Ag(CN)_2'$ and $Zn(CN)_4''$.

Owing to the extreme weakness of hydrocyanic acid, $K = 4\cdot5 \times 10^{-10}$, it is only able to form soluble salts, which ionise in a normal manner, with strong bases, *e.g.*, NaOH. Mercuric cyanide is, however, soluble, but in solution it is almost completely un-ionised (see p. 96). The hydrogen-ion concentrations of solutions of hydrocyanic acid are much too small

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to effect the dissolution of such weak bases as ferric hydroxide. For instance, the acid is incapable of establishing a pH value of 2, at which the base begins to precipitate from ordinary solutions ; yet, in conjunction with alkali cyanides, ferric hydroxide combines with hydrocyanic acid in the form of well-defined and readily soluble salts.   Such salts are usually regarded as those of complex acids, and this view is supported by the fact that electrical transference experiments indicate that the weak base exists in the complex anion.   On the other hand, it is not an easy matter to establish the composition of the complex ion as it exists in solution, and it is in this regard that the investigation of the pH of solutions containing complex cyanide anions bv Britton and Dodd (*J. Chem.* has proved of service.

Hydrolysis of Alkali Cyanides and Complex Cyanides.

An ingenious method of estimating the small concentrations of hydrolysed hydrocyanic acid was introduced by Worley and Brown (*J. Chem. Soc.*, 1917, **111**, 1057) and was later used by Harman and Worley (*Trans. Faraday Soc.*, 1924, **20**, 502) and Britton and Dodd (*loc. cit.*).   The method is as follows :—

Air is drawn through a flask containing a solution of the cyanide undergoing test and is thereafter bubbled through 10 c.c. of a 0·2 per cent. solution of picric acid in 2 per cent. sodium carbonate, contained in a test-tube.   This is connected in series with a flask, containing a volume (equal to that of the complex cyanide solution) of hydrocyanic acid solution of a suitable concentration, and a test-tube of sodium picrate solution.   After air has been bubbled through the apparatus very slowly for about 30 minutes, the tubes containing the picrate solution are removed and placed in boiling watei for 2–3 minutes.   This causes brown colours to be developed, the intensities of which are dependent on the amounts of hydrocyanic acid absorbed, and consequently on the amounts of free hydrocyanic acid in the two cyanide solutions.   Trials are performed with different known concentrations of hydrocyanic acid until a known and a test picrate solution produce colours of the same intensity when compared by means of the light emitted by a Mazda " daylight lamp." The apparatus is completely immersed in an electrically regulated thermostat at 25·0° and the air used is previously passed through a long tube, packed with soda-lime.

Table 194 gives some results obtained by means of this method by Britton and Dodd, with solutions of potassium cyanide at 25°.

TABLE 194

Conc. KCN, M.	HCN hydrolysed, per cent.	$K_h \times 0^5$.	$K_{HCN} \times 10^{10}$.
0·245	1·00	2·50	5·01
0·098	1·59	2·51	5·01
0·049	2·29	2·62	4·79
0·0245	3·18	2·56	4·90
		Mean 2·55 × 10⁻⁵	4·93 × 10⁻¹⁰

They also applied the method to the study of solutions of complex cyanides and some of their results are recorded in Table 195. Solutions were also investigated which contained various ratios of potassium cyanide. Using the hydrolysis constant, K_h, given in the foregoing table, the concentrations of hydrocyanic acid which originated from the excess potassium cyanide were calculated, it being assumed that the complex cyanide was unhydrolysed. The difference between the observed and calculated concentrations gave the concentrations which had hydrolysed from the complex cyanide, from which the percentage hydrolysis of the complex salt was computed.

TABLE 195

		Conc., M.		Conc. HCN M. × 10⁴.		Per cent. Hydrolysis of Complex.
		Complex Cyanide.	KCN.	Obs.	Calc.	
$KAg(CN_2)$	—	0·0933	0	0	0	0
,,	—	0·0320	0	0	0	0
,,	—	0·0082	0	0	0	0
,,	+ 2·00 KCN	0·0197	0·0393	9·9	9·9	0
,,	+ 3·98 ,,	0·0141	0·0562	11·9	11·8	+ 0·02
,,	+ 8·00 ,,	0·0089	0·0714	13·2	13·3	− 0·06
,,	+ 11·98 ,,	0·0066	0·0785	13·8	14·0	− 0·16
$K_2Zn(CN)_4$	—	0·0198	0	3·8	0	0·50
,,	+ 1·00 KCN	0·0165	0·0165	9·0	6·4	0·40
,,	+ 1·99 ,,	0·0149	0·0297	10·5	8·6	0·33
,,	+ 3·90 ,,	0·0116	0·0451	10·8	10·6	0·04
,,	+ 5·99 ,,	0·0095	0·0567	11·9	11·9	0·00
$K_2Cd(CN)_4$	—	0·0245	0	5·0	0	0·53
,,	+ 1·00 KCN	0·0196	0·0196	9·1	6·9	0·28
,,	+ 2·00 ,,	0·0167	0·0347	11·0	9·3	0·26
,,	+ 4·00 ,,	0·0115	0·0460	11·2	10·7	0·11
,,	+ 6·00 ,,	0·0094	0·0565	11·8	11·8	0·00
$K_2Ni(CN)_4$	—	0·0201	0	0	0	0
,,	+ 1·00 KCN	0·0167	0·0168	7·8	6·4	0·21
,,	+ 2·01 ,,	0·0143	0·0288	9 8	8·4	0·24
,,	+ 4·00 ,,	0·0114	0·0456	10·6	10·6	0·00
,,	+ 6·00 ,,	0·0094	0·0565	11·8	11·9	− 0·02
$K_4Fe(CN)_6$	—	0·1000	0	0	0	0
,,	+ 1·00 KCN	0·0253	0·0253	7·8	7·9	− 0·01
,,	+ 2·00 ,,	0·0170	0·0339	9·2	9·2	0
,,	+ 4·00 ,,	0·0102	0·0409	10·0	10·1	− 0·01
,,	+ 6·00 ,,	0·0073	0·0438	10·5	10·4	+ 0·01

Comparison of the figures given in the last column of Table 195 with the values given in Table 194 shows that all the complex cyanides undergo considerably less hydrolysis than potassium cyanide alone, and that as the ratio of potassium cyanide is increased the complex anions become even more stable, as indicated by the suppression of their hydrolysis.

No trace of hydrolysis was found in freshly prepared solutions of potassium ferricyanide and cobalticyanide, but when solutions containing free potassium cyanide were made up, hydrocyanic acid was liberated far in excess of that due to hydrolysis of the potassium cyanide. It is probable that this hydrolysis is caused by the weakness of ferric and cobaltic hydroxides as bases and their consequent difficulty of being retained completely in complex formation in solutions of high pH, such as is set up by an excess of potassium cyanide.

The weakness of mercuric oxide as a base might also explain why potassium mercuricyanide, $K_2Hg(CN)_4$, although it alone undergoes slight hydrolysis, becomes increasingly hydrolysed as the excess of potassium cyanide is increased (*loc. cit.*).

Similar measurements were made on potassium cyanide solutions of cuprous cyanide and auric cyanide by Britton and Dodd , which effectively proved the existence of slightly hydrolysed complex cyanides, *viz.*, $K_2Cu(CN)_3$ and $KAu(CN)_4$, in solution.

In view of the relatively small hydrolysis of complex cyanides compared with that of potassium cyanide, it was considered that the variation in pH produced when potassium cyanide is progressively added to metallic salt solutions might throw some light on the composition of any complex salts that may result therefrom. For the purpose, the glass electrode is admirably suited. Fig. 148 gives some of the curves thus obtained (Britton and Dodd, They refer to the titration of 100 c.c. of approximately 0·001 M. solutions of the sulphates of zinc, cadmium and nickel, mercuric chloride, silver nitrate and sodium chloro-aurate with 0·1 M. potassium cyanide. The curve, marked CuCN, is that of cuprous cyanide suspended in water to which increasing amounts of potassium cyanide were added.

Direct titrations showed that in some cases redissolution of the precipitated simple cyanide in excess potassium cyanide was very slow, and hence equilibrium values of the pH of the solution could not be obtained. To obviate this difficulty, mixtures of the metallic salt solution with various amounts of potassium cyanide were placed in bottles, which were shaken for several hours

or kept over-night, before the pH of the solution was measured. By this means steady and reproducible pH values were obtained.

The uppermost curve in Fig. 148, labelled KCN, represents the pH values which would have been set up if the reactions of the various salts with potassium cyanide had consisted simply of double decompositions and the excess of the potassium cyanide had remained, as such, in solution. In no instance was this the case, including the reaction with mercuric chloride, the curve of which possesses no inflexion corresponding to the formation of $K_2Hg(CN)_4$, which is undoubtedly formed.
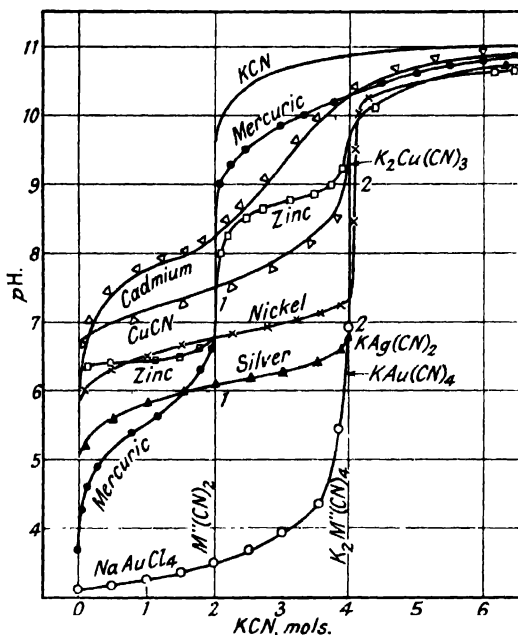
FIG. 148.—Glass Electrode Titrations of Solutions of Metal Salts with Potassium Cyanide.

The final inflexions, occurring when 4 molecules of KCN had been added (2 molecules in the case of CuCN and AgNO₃), clearly indicate the formation of $K_2Zn(CN)_4$, $K_2Ni(CN)_4$, $KAg(CN)_2$, $K_2Cu(CN)_3$ and $KAu(CN)_4$. The cadmium curve does not lead to such a definite conclusion. At this stage, the metallic cyanide precipitates had completely dissolved. Further proof was obtained by calculating the ratio [CN']/[HCN] from the pH of solutions containing an excess of KCN by the equation

$$p\mathrm{H} = p\mathrm{K}_{\mathrm{HCN}} + \log [\mathrm{CN'}]/[\mathrm{HCN}],$$

and then, knowing the concentration of free hydrocyanic acid, liberated by hydrolysis and determined by the picric acid vapour pressure method, it was possible to calculate the cyanide-ion concentration. The concentrations. thereby obtained corresponded closely with that of the uncombined potassium cyanide, *i.e.*, in excess of that necessary to form the various complex cyanides indicated by the curves. Table 196 gives typical results of such computations—in this case, referring to the formation of $K_2Ni(CN)_4$ by the interaction of $NiSO_4$ and KCN.

TABLE 196

Conc., M × 10⁴.		pH.	$\frac{[CN']}{[HCN]}$	[HCN] × 10⁴.		[HCN] × 10⁴.	[CN'] × 10³.	[CN'] [KCN].
K₂Ni(CN)₄.	KCN.			Complex.	KCN.			
9·09	4·54	10·34	10·47	0·36	3·23	3·59	3·76	0·8
9·09	9·09	10·52	15·85	0 76	4·55	5·31	8·42	0·9
9·09	13·63	10·66	21·88	0·80	5·59	6·39	13·98	1·0
9·09	18·18	10·78	28·84	0·87	6·36	7·23	20·86	1·1

Britton and Dodd (*J. Chem. Soc.*, 1933, 1543) also carried out a glass electrode titration of hydroferrocyanic acid with alkali. The *p*H curve is that of a strong acid in each of its four stages of ionisation and the end of the neutralisation, giving $Na_4Fe(CN)_6$, is well defined. It is not quite as strong as sulphuric acid (cf. Malaprade, *Ann. Chim.*, 1929, **11**, 136).

Complex Silver Ammine Cations

The precipitation of silver oxide from silver nitrate solution by ammonia and its subsequent re-solution have been studied from various points of view. Prescott (*Chem. News*, 1880, **42**, 31), Reychler (*Ber.*, 1883, **16**, 990), Draper (*Pharm. J.*, 1886, **17**, 488), and Herz (*Z. anorg. Chem.*, 1910, **67**, 248) found that when approximately 2 molecules of ammonia were added to 1 molecule of silver nitrate the precipitate first formed redissolved. That the substances in these proportions do enter into some kind of reaction has been shown by the following physicochemical methods : cryoscopy and conductivity (Reychler, *Ber.*, 1883, **16**, 2421 ; 1895, **28**, 555), measurements of partial pressure of ammonia (Konowalov, *Z. physikal. Chem.*, 1898, **28**, 558 ; Gans, *Z. anorg. Chem.*, 1900, **25**, 236), thermo-chemical measurements (Berthelot and Delépine, *Compt. rend.*, 1899, **129**, 326 ; Bruni and Levi, *Gazzetta*, 1917, **47**, i, 259), E.M.F., and transference number

determinations (Whitney and Melcher, *J. Amer. Chem. Soc.*, 1903, **25**, 70). The current view that silver exists in ammoniacal solutions as a complex cation, each silver atom being associated with two molecules of ammonia, originated in the work of Bodländer and Fittig (*Z. physikal. Chem.*, 1901, **39**, 597), who showed by an application of the mass law that the solubility of silver chloride in ammonia could be accounted for if the silver were assumed to pass into a complex ion, $Ag(NH_3)_x$, the values of x actually varying from 1·67 to 2·22.

Britton (*J. Chem. Soc.*, 1925, **127**, 2956) followed the pH, as indicated approximately by the oxygen electrode, and the silver-ion concentration as ammonia is added to a solution of silver nitrate and concluded that the complex salt, $Ag(NH_3)_2NO_3$, is formed as soon as 2 molecules of ammonia are added to 1 molecule of silver nitrate. He also showed that the E.M.F. data, obtained with the silver electrode by Bruni and Levi in solutions of either silver nitrate or silver nitrite containing varying amounts of ammonia could be explained satisfactorily by assuming the formation of the complex cation, $Ag(NH_3)_2$. The fact that strong bases, *e.g.*, sodium hydroxide, are unable to precipitate silver oxide from solutions of the complex silver salt suggests that salts of the type, $Ag(NH_3)_2NO_3$, must be the salts of a base, apparently $Ag(NH_3)_2OH$, which is comparable in strength with that of sodium hydroxide. This has been shown to be the case by Britton and Wilson (*J. Chem. Soc.*, 1933, 1050) and Britton and Williams (*ibid.*, 1935, 796) by means of the glass electrode ; the complex base being formed when silver oxide dissolves in aqueous solutions of ammonia. They showed that similar complex bases are formed by dissolving silver oxide in aqueous solutions of substituted ammonias, and that the complex salts are formed by adding various organic bases to silver nitrate in solution (*ibid.*, 1936, 96).

Reactions between Silver Nitrate and Ammonia and Organic Bases.

The upper curves in Fig. 149 illustrate the variation in pH at 18° C., measured by means of the glass electrode when the bases indicated are added to silver nitrate in solution. The lower curves give the corresponding changes in pAg, *i.e.*, $-\log_{10}[Ag\cdot]$. The solutions used were 100 c.c. 0·22 N-$AgNO_3$ titrated with 0·1 N-ammonia, 0·0896 N-diethylamine, 0·102 N-triethylamine, 0·09775 N-ethylamine, 0·0953 N-methylamine, and 0·225 N-ethylenediamine respectively. Partial precipitation of silver oxide occurred with ammonia, it reached a maximum with 1 molecule

and re-dissolved completely when 2 molecules (per molecule of AgNO$_3$) had been added.

The curves, marked NH$_2$Et + NH$_2$Et,HNO$_3$ and

NH$_2$Me + NH$_2$Me,HNO$_3$,

refer to glass electrode and silver electrode titrations of 100 c.c. of (*i*) 0·2 N-AgNO$_3$ + 0·1013 N-NH$_2$Et,HNO$_3$ with 0·09775
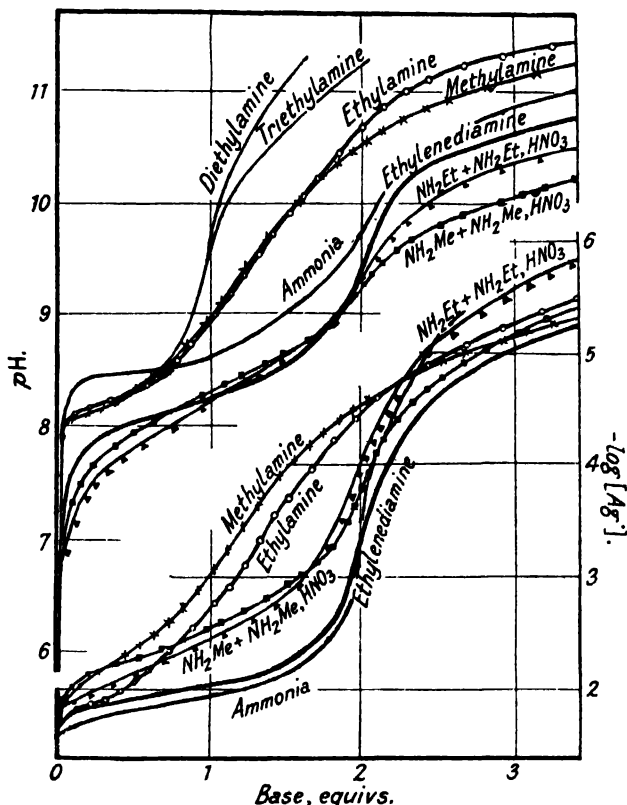
FIG. 149.—Glass Electrode Titrations of Silver Nitrate with Ammonia and Organic Bases.

N-ethylamine and (*ii*) 0·02 N-AgNO$_3$ + 0·063 N-NH$_2$Me,HNO$_3$ with 0·0953 N-methylamine respectively. The inclusion of these salts prevented the precipitation of Ag$_2$O, and this is reflected in the appearance of better defined inflexions when two equivalents of each of the bases had been added. They show that owing to the repression of the ionisation of the added bases by the cations

originating from the respective salts, the un-ionised bases become more susceptible to forming complex cations. Similar observations have been made when ammonium hydroxide is added to solutions of silver nitrate in the presence of ammonium nitrate. A faint opalescence was soon formed in the ethylenediamine titration, but disappeared immediately 2 equivalents had been added. In the first two cases, therefore, and also in that of ethylenediamine, the silver must have been held in solution in the form of complex cations : this is reflected in the titration curves by the inflexions with 2 equivalents of the bases.

The addition of di- and tri-ethylamine caused extensive precipitation of silver oxide, as indicated by the appearance of well-defined inflexions with 1 equivalent of each base. With both ethylamine and methylamine the precipitation was less : the curves have inflexions extending from 1 to 2 equivalents.

The silver electro-titration curves (lower part of Fig. 149), which refer to the solutions and titrants of the same concentrations as above, have similar characteristics. The ethylenediamine curves bring out clearly the fact that the complex salt involves one molecule of the base,

$$AgNO_3 + C_2H_4(NH_2)_2 \rightarrow Ag[C_2H_4(NH_2)_2]NO_3.$$
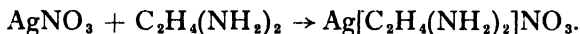
(The complex cation is usually represented by Agen, see, however, Traube, *Ber.*, 1911, **44**, 3320).

The proportion of silver oxide precipitated at various stages of the titrations was determined by precipitation of the silver in solution as chloride. To 100 c.c. of 0·02 N-silver nitrate various amounts of base were added, mechanically shaken for some time at room temperature, and the silver in the liquid phase estimated. The results are plotted in Fig. 150, in which are also curves showing the percentage of silver oxide precipitated when 0·1 N- and 1·0 N-silver nitrate solutions are treated with ammonia (see Britton and Wilson, *J. Chem. Soc.*, 1933, 1050). The broken line represents the normal precipitation of silver oxide with sodium hydroxide. Unlike ammonia, none of the organic bases causes the silver oxide to redissolve when 2 molecules of base per molecule of silver nitrate have been added. Reychler (*Ber.*, 1883, **16**, 990) and Herz (*Z. anorg. Chem.*, 1910, **67**, 248) considered the ratio 2 : 1 to indicate formation of the complex cation, $Ag(NH_3)_2^{\cdot}$, but, as the following considerations show, such a ratio is fortuitous in that the precise ratio depends on the three factors :—The instability constant of the complex cation, $AgB_2^{\cdot}$, the solubility product of silver hydroxide, and the dissociation constant of the organic base. The following considerations satisfactorily account for the precipitation data plotted in Fig. 150.

When a base, B, is added to silver nitrate, two reactions occur simultaneously : (i) the partial precipitation of silver oxide, (ii) the conversion of some silver nitrate into the complex nitrate, AgB_2NO_3. These two reactions bring into play the equilibria

$$AgB_2^{\cdot} \rightleftharpoons Ag^{\cdot} + 2B, \quad B + H_2O (= BHOH) \rightleftharpoons BH^{\cdot} + OH',$$

and $\quad$ AgOH (solid) $\rightleftharpoons$ AgOH (dissolved) $\rightleftharpoons Ag^{\cdot} + OH'$,

which are governed by the respective expressions

$$K_1 = \frac{[Ag^{\cdot}][B]^2}{[AgB_2^{\cdot}]} ; \quad K_b = \frac{[BH^{\cdot}][OH']}{[B]} ; \quad L = [Ag^{\cdot}][OH'],$$

whence $\qquad K_1 . K_b^2/L^2 = [BH^{\cdot}]^2/[Ag^{\cdot}][AgB_2^{\cdot}] \quad . \quad . \quad . \quad (1)$

and $\qquad K_1 . K_b /L = [BH^{\cdot}][B]/[AgB_2^{\cdot}] \quad . \quad . \quad . \quad . \quad (2)$
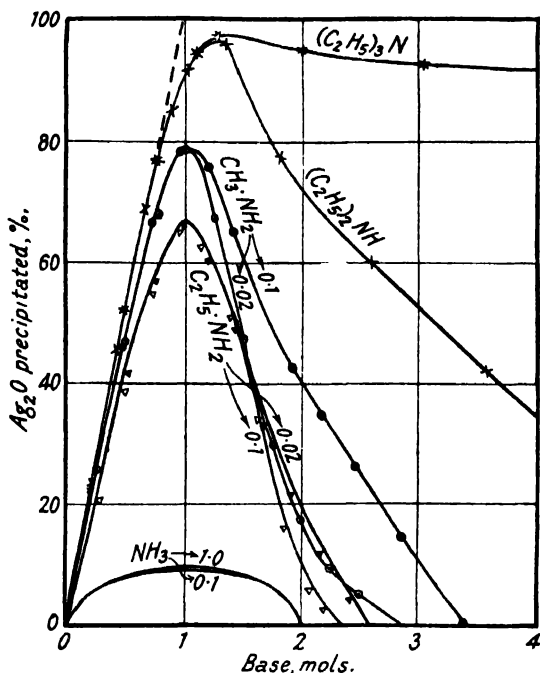
FIG. 150.—Percentage Ag_2O precipitated with Varying Amounts of Ammonia and Organic Bases.

Equation (1) is applicable particularly to the first stage of the reaction of the base with silver nitrate, *i.e.*, when there' is an appreciable silver-ion concentration originating from any un-attacked silver nitrate (Case I), and equation (2) refers to the second stage where some of the added base has failed to react,

either in precipitating silver oxide or in forming the complex salt, AgB_2NO_3 (Case II). From a knowledge of the three constants involved, it is possible to calculate the extents to which the base has reacted in (a) precipitating silver oxide and (b) complex formation. Thus, let the original concentration of silver nitrate be c, and the total concentration of added base $2a$; of the silver nitrate reacted upon, suppose a fraction, x, yielded an equivalent quantity of silver oxide.

Case I

$$2axBHOH + 2axAgNO_3 = 2axB,HNO_3 + 2axAgOH$$
$$2a(1 - x)B + a(1 - x)AgNO_3 = a(1 - x)AgB_2NO_3.$$
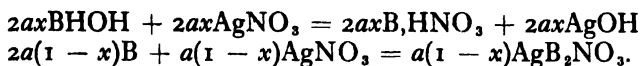
The complete ionisation of B,HNO_3, AgB_2NO_3, and any unattacked $AgNO_3$ being assumed, it follows that $[BH^\cdot] = 2ax$, $[AgB_2^\cdot] = a(1 - x)$, and $[Ag^\cdot] = \{c - a(1 - x) - 2ax\}$, whence

$$K_1 . K_b^2/L^2 = 4ax^2/(c - a - ax)(1 - x)$$

from which, the fraction of silver oxide precipitated, $viz.$, $2ax/c$, can be calculated.

Case II

$$2c(1 - x)B + c(1 - x)AgNO_3 = c(1 - x)AgB_2NO_3$$
$$xcBHOH + xcAgNO_3 = xcB,HNO_3 + xcAgOH$$
$$[BH^\cdot] = xc, \quad [B] = \{2a - xc - 2c(1 - x)\}, \quad [AgB_2^\cdot] = c(1 - x).$$
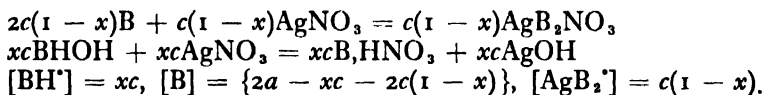
Hence
$$\frac{K_1 . K_b}{L} = \frac{x(2a + xc - 2c)}{1 - x}$$

and the fraction of silver oxide precipitated is $xc/c = x$.

If aniline and pyridine did not enter into complex formation with silver ions, then, despite their weakness as bases, they should, when added in sufficient excess to silver nitrate solution, be able to set up pH values which would cause the precipitation of some silver oxide. Complex cations (Britton and Williams, $loc.$ $cit.$), are formed, however, and consequently no silver oxide is precipitated.

Solutions of Silver Oxide in Ammonia and Amines.

Fig. 151 summarises the solubility of silver oxide in solutions of ammonia and various substituted ammonias at 15° obtained by Whitney and Melcher, ($J.$ $Amer.$ $Chem.$ $Soc.$, 1903, **25**, 87); Euler, ($Ber.$, 1903, **36**, 1854); Olmer, ($Bull.$ $Soc.$ $chim.$, 1924, **35**, 333) and Britton and Williams ($J.$ $Chem.$ $Soc.$, 1935, 796).

The nature of these solutions will be understood from a study of Fig. 152, which gives a series of glass electrode titration curves

and parallel conductometric titration-curves. The glass electro-titrations were carried out at 18° with the following solutions

A, 50 c.c. of 0·0298 M.-Ag(NH₃)₂OH + 0·0376 N-NH₄OH, titrated with 0·2078 N-HNO₃ ;

B, 50 c.c. of 0·03920 M.-Ag(NH₂Me)₂OH + 0·0825 M.-NH₂Me, titrated with 0·3380 N-HNO₃ ;
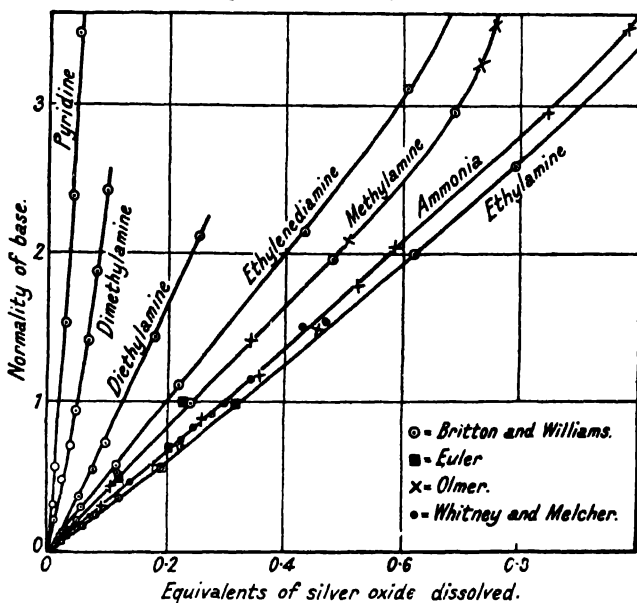
FIG. 151.—Solubility of Ag₂O in Solutions of Ammonia and Organic Bases.

C, 50 c.c. of 0·03084 M.-Ag(NH₂Et)₂OH + 0·03084 M.-NH₂Et, titrated with 0·1928 N-HNO₃ ;

D, 50 c.c. of 0·02842 M.-Ag en OH + 0·04618 M.-C₂H₈N₂, titrated with 0·2368 N-HNO₃ ;

E, 50 c.c. of 0·0034 M.-AgPy₂OH + 0·2106 M.-pyridine, titrated with 0·3368 N-HNO₃ ;

F, 50 c.c. of 0·0034 M.-AgPy₂OH + 0·2106 M-pyridine, titrated with 0·0129 N-HNO₃.

The conductometric curves, A, B, C, D, were obtained by titrating 100 c.c. of the above solutions with the same titrant at 25°.

Both types of curve demonstrate the formation of a strong base of the general formula Ag(B)₂OH, becoming Ag en OH in the case of ethylenediamine. The curves may be divided into three sections, denoted by Roman numerals, corresponding to

the addition of various amounts of nitric acid : I relates to the neutralisation of the strong complex base ; II to that of the ammonia or amine in excess of that required to form the complex base ; and III to the decomposition of the complex nitrate,
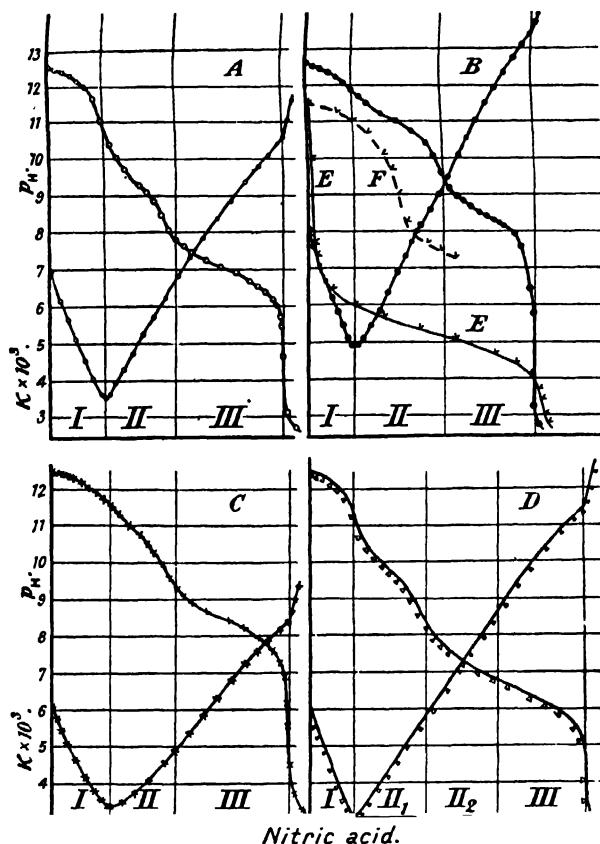
FIG. 152.—Glass Electrode and Conductometric Titrations of Ag_2O in Solutions of Ammonia and Amines.

$Ag(B)_2NO_3$ (B $=$ unhydrated base), formed at the end of stage I, into silver nitrate and the nitrate of the simple base :

$$AgB_2NO_3 + 2HNO_3 \rightleftharpoons AgNO_3 + 2BHNO_3,$$

or $\qquad AgB_2^{\cdot} + 2H^{\cdot} \rightleftharpoons Ag^{\cdot} + 2BH^{\cdot}.$
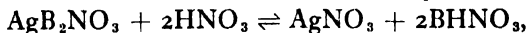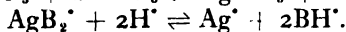
Hence $\qquad [Ag^{\cdot}][BH^{\cdot}]^2 / [AgB_2^{\cdot}][H^{\cdot}]^2 = K \quad . \quad . \quad . \quad (1)$

and as $\qquad B + H_2O \rightleftharpoons BHOH \rightleftharpoons BH^{\cdot} + OH',$

therefore $\qquad [BH^{\cdot}][OH'] / [BHOH] = K_b.$

If it is assumed that the undissociated base is also unhydrated, *e.g.*, that undissociated ammonium hydroxide molecules exist in solution simply as molecules of ammonia (see, *e.g.*, Calingaert and Huggins, *J. Amer. Chem. Soc.*, 1923, **45**, 915), and similarly that the undissociated substituted ammonia molecules exist as such, then the concentration of the base, [B], is equal to that of the undissociated base, [BHOH],

whence $$[BH^{\cdot}][OH']/[B] = K_b \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Combination of equations (1) and (2), and introduction of $K_w = [H^{\cdot}] \times [OH']$, give

$$[Ag^{\cdot}][B]^2/[AgB_2^{\cdot}] = K \cdot K_w^2/K_b^2 = K_I$$

where K_I is the instability constant of the complex cation in question. It is seen therefore that the *p*H during stage III depends on the instability constant of the complex cation and the dissociation constant of the base which it incorporates.

That two equivalents of the bases combine with one of silver is apparent from the fact that the amount of nitric acid used in stage III is exactly twice the amount required in stage I. Because methylamine and ethylamine are somewhat stronger bases than ammonia, stage II in B and C tends to merge into stage I without a well-defined inflexion. The termination of the neutralisation of the strong complex methylamino- and ethylamino-silver bases is, however, clearly indicated in the conductometric curves, sharp " breaks " being obtained. No further breaks were obtained until the complex ions had been entirely decomposed and free nitric acid began to be present in the solutions. This is to be ascribed to the fact that the mobilities of the cations involved do not differ greatly from one another.

Although the solubility of silver oxide in pyridine is very small, the high *p*H values indicated during the initial portions of curves E and F in Fig. 152 show that the complex pyridine base is quite strong.

The equivalent conductivities of the complex bases and their apparent degrees of ionisation, α, given in Table 196 show that the complex bases, like the silver-ammonia base, are very strong.

The values of α were calculated from the *p*H values, allowances being made for the concentrations of hydroxyl ions originating from the excess of the organic bases ; α thus represents

(Concentration of hydroxyl ions from complex base)

(Concentration of complex base)

It is possible to explain the solubility of silver oxide in solutions of ammonia and amines, in forming strong complex bases, AgB_2OH, in terms of the instability constant of the complex

TABLE 196

Base.	G.-equivs. per Litre.		$\kappa \times 10^3$.	Λ.	pH.	a.
	Base.	Ag$_2$O.				
Ammonia . . .	0·0972	0·0298	—	—	12·57	0·90
Methylamine . .	0·1007	0·02338	4·64	189	12·48	0·78
Ethylamine . . .	0·1210	0·03805	7·54	194	12·66	0·72
Ethylenediamine .	0·1162	0·02369	4·85	202	12·47	0·78
Pyridine	0·2233	0·0034	0·620	201	11·58	0·76

cation formed, and the solubility product of silver hydroxide, or conversely to calculate the instability constant of the complex cation. Thus, let the concentration of base be C g.-equivs. per litre, and the amount of silver hydroxide dissolved be S g.-equivs. per litre. This is equal to the concentration of the complex base, AgB$_2$OH. The concentration of base which co-ordinates with the silver hydroxide is 2S, and consequently the concentration of free base is C − 2S. Hence, if the degree of ionisation of the complex base, AgB$_2$OH, is α, then

$$[Ag^\bullet][B]^2/[AgB_2^\bullet] = K_I = [Ag^\bullet](C - 2S)^2/\alpha S,$$

and as the solution is saturated with respect to silver oxide, $[Ag^\bullet][OH'] = L$; whence $K_I = L(C - 2S)^2/\alpha S[OH']$, and as $[OH']$ originates from the ionisation of the complex base, $[OH'] = \alpha S$, and therefore $K_I = L(C - 2S)^2/\alpha^2 S^2$.

Hence $C = S(2 + \alpha\sqrt{K_I/L})$, and consequently, if α is either unity or else constant, the solubility of silver oxide should be directly proportional to the concentration of the organic base as is shown by the curves in Fig. 151.

There appears to be no relationship between the strength of the base and the stability of the resulting complex cations. For instance, both dimethylamine and diethylamine are stronger than either ammonia or their respective primary bases, yet the instability constants of the dialkylaminosilver cations are appreciably greater, and although pyridine is so very much weaker as a base than either of the tertiary bases trimethylamine and triethylamine, yet the pyridinosilver cation is slightly more stable than the other two.

As far as can be ascertained from the instability constants, except for the complex aniline cation, complex cations involving ammonia or primary amines are more stable than those involving secondary amines, which in turn are more stable than those involving tertiary bases. In other words, the order of the co-ordinating tendencies with regard to silver is primary > secondary > tertiary amines.

CHAPTER XXX

ANALYTICAL PROCESSES INVOLVING pH

IN this chapter attention will be directed to a number of analytical processes in which hydrogen-ion concentration and its control play an important part.

Sørensen's Formol Titration.

Sørensen (*Biochem. Z.*, 1907, **7**, 45) found that if an excess of neutralised formaldehyde be added to a solution of an ampholyte it becomes possible to titrate the carboxyl group to phenolphthalein. Thus for glycine, $K_a = 1·8 \times 10^{-10}$, only a slight, indefinite, inflexion will occur in the pH curve at pH 11–12 on neutralisation with alkali. Volumetric titration is not, therefore, practicable, but in the presence of sufficient formaldehyde K_a is increased to 4×10^{-6} and consequently at pH 7·4 the neutralisation of the carboxyl group is effectively at an end. Phenolphthalein thus becomes a suitable indicator. Harris (*Proc. Roy. Soc.*, 1925, **97**, B, 357; 1929, **104**, B, 412; see also Birch and Harris, *Biochem. J.*, 1930, **24**, 1080) observed that the increase in strength of the amino-acid depends on the concentration of the formol, the maximal increases being 1000- to 10,000-fold. This applies only to very weak acids, the constants of which are of the order of 10^{-9} to 10^{-10}. The second stage of the acid-ionisation of tyrosine is extremely weak, $K_{a_1} = 4 \times 10^{-11}$. In the presence of formaldehyde, this stage increases to about 10^{-9}. Regarding amino-acids which contain fairly strongly dissociating carboxyl groups, *e.g.*, the first stages of ionisation of glutamic, $K_{a_1} = 4 \times 10^{-5}$, and of aspartic acids, $K_{a_1} = 1·5 \times 10^{-4}$, it should be mentioned that formaldehyde also increases their strength, but only to the extent of about 10 times.

It was considered by Sørensen that these increases in acid strength were to be attributed to the introduction of methylene-imino groups in the place of amino groups, thus reducing any influence which they may have on the dissociation of the carboxyl groups. This, however, is not the case, for amino groups may react with 2 molecules of HCHO and possibly with three. Imino groups, such as are present in sarcosine and proline, combine only with one (Balson and Lawson, *Biochem. J.*, 1936, **30**,

1257; Tomiyama, *J. Biol. Chem.*, 1935, **111**, 51; Levy and Silberman, *ibid.*, 1937, **118**, 723). Balson and Lawson suggest the following explanations of the reactions with :—

(*a*) *imino group*, $=NH + HCHO \rightarrow =N\text{-}CH_2OH$

(*b*) *amino group*,

$$-NH_2 + HCHO \quad\quad \rightarrow -NH.CH_2OH$$
$$-NHCH_2OH + HCHO \rightarrow -N(CH_2OH)_2$$
$$-N(CH_2OH)_2 + HCHO \rightarrow -N\overset{CH_2O}{\underset{CH_2O}{\Big\langle}}\!\!\Big\rangle CH_2 + H_2O.$$
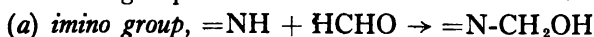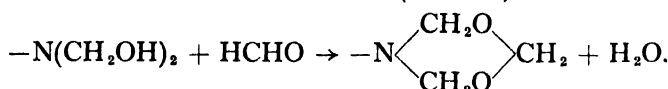
The method adopted by Balson and Lawson and by Levy and Silberman in reaching these conclusions is essentially that described below.

Suppose that a weak amino-acid, HR, combines respectively with 1, 2 and 3 molecules of formaldehyde, F, to form

$$HRF, HR_2F \text{ and } HR_3F.$$
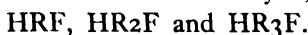
Let

$$K_a = \frac{[H^{\cdot}][R']}{[HR]},$$

which thus refers to the dissociation of the acid in the absence of formalin, and let K_0 be the apparent dissociation constant when the concentration of formaldehyde is [F].

Hence

$$K_0 = \frac{[H^{\cdot}](\text{Total concentration of anions})}{(\text{Total concentration of Undissociated acids})}$$

$$= \frac{[H^{\cdot}].([R'] + [RF'] + [R_2F'] + [R_3F'])}{[HR] + [HRF] + [HR_2F] + [HR_3F]}$$

Let

$$K_1 = \frac{[H^{\cdot}][RF']}{[HRF]}, \text{ for } HRF \rightleftharpoons H^{\cdot} + RF',$$

$$K_2 = \frac{[H^{\cdot}][R_2F']}{[HR_2F]}, \text{ for } HR_2F \rightleftharpoons H^{\cdot} + R_2F'',$$

and

$$K_3 = \frac{[H^{\cdot}][R_3F']}{[HR_3F]}, \text{ for } HR_3F \rightleftharpoons H^{\cdot} + R_3F'.$$

Applying the law of mass action to the three successive association equilibria, we obtain for—

$$R' + F \rightleftharpoons RF', \quad A_1 = \frac{[RF']}{[R'].[F]}$$

$$RF' + F \rightleftharpoons R_2F'', A_2 = \frac{[R_2F']}{[RF'].[F]}$$

$$R_2F'' + F \rightleftharpoons R_3F, \quad A_3 = \frac{[R_3F']}{[R_2F'].[F]}.$$

By combining these seven expressions with the expression for K_0, we get

$$\left(\frac{K_0}{K_a} - 1\right) + \left(\frac{K_0}{K_1} - 1\right)A_1[F] + \left(\frac{K_0}{K_2} - 1\right)A_1A_2[F]^2$$
$$+ \left(\frac{K_0}{K_3} - 1\right)A_1A_2A_3[F]^3 - 0.$$

If $\dfrac{K_0}{K_1}$, $\dfrac{K_0}{K_2}$ and $\dfrac{K_0}{K_3}$ are each negligible compared with unity, then

$$\left(\frac{K_0}{K_a} - 1\right) = A_1[F] + A_1A_2[F]^2 + A_1A_2A_3[F]^3$$

i.e., $$\frac{K_0}{K_a} = 1 + A_1[F] + A_1A_2[F]^2 + A_1A_2A_3[F]^3.$$

For an amino-acid which combines with one molecule of formaldehyde, the expression,

$$\frac{K_0}{K_a} = 1 + A_1[F],$$

should hold, whereas it becomes

$$\frac{K_0}{K_a} = 1 + A_1[F] + A_1A_2[F]^2,$$

when two molecules have successively combined. Balson and Lawson determined, with the hydrogen electrode, the variation in K_0 by measuring the pH of a solution of a half-neutralised amino-acid to which formaldehyde was progressively added. (*i.e.*, pH $= p$K$_0$). By plotting $\left(\dfrac{K_0}{K_a} - 1\right) / [F]$ against $[F]$ as abscissa, they obtained a horizontal line in the case of sarcosine and proline, showing that one molecule only of formalin combines with each of the ampholytes. In the case of acids containing $-NH_2$ groups, straight lines, which would have been expected if two molecules had reacted, were not obtained. Instead, the curves were slightly parabolic, suggesting that a third molecule of formalin had been involved. Levy and Silberman, however, by plotting K_0 against log $[F]$, agree that with all imino acids and tryptophan one molecule only of formol reacts, whereas they conclude that two molecules unite with amino acids.

Provided that the formalin is neutralised to pH 7, there is no need to apply a correction for the acidity of the formaldehyde used in formol titrations. Maximum accuracy appears to be obtained when the concentration of formaldehyde is 6 to 9 per cent. when the end-point is reached.

Table 197 gives the values of pK_0 of amino- and imino-acids at 30° compared with pK_a. The data are taken from the paper of Levy and Silberman (*loc. cit.*), see also Dunn and Loshakoff (*J. Biol. Chem.*, 1936, 113, 359, 691).

TABLE 197

ACID DISSOCIATION CONSTANTS OF AMPHOLYTES AND THEIR APPARENT VALUES IN 9 PER CENT. HCHO SOLUTION AT 30°

Ampholyte.	pK_a.	pK_0
Glycine .	9·60	5·70
dl-Alanine .	9·72	6·86
l-Leucine .	9·50	6·92
dl-Valine .	9·50	7·25
dl-α-Aminophenyl acetic acid .	8·84	5·95
l-Phenylalanine	8·09	6·62
l-Tyrosine .	9·07	7·70
l-Tryptophan .	9·27	6·88
l-Proline .	10·30	7·78
l-Hydroxyproline .	9·56	7·19
dl-Sarcosine .	10·06	7·41
d-Lysine .	10·56	7·15
d-Arginine .	8·91	3·40
l-Histidine .	9·17	7·90
d-Glutamic acid (pK_{a_2}) .	9·32	6·91
l-Aspartic acid (pK_{a_2}) .	9·83	7·21

Titration of Boric Acid.

Boric acid behaves as an extremely weak monobasic acid, HBO_2,H_2O, $K = 6 \times 10^{-10}$, and therefore gives an indefinite end-point in the region of pH 11, and, as may be seen from the titration curve in Fig. 153, will cause phenolphthalein to turn colour when the acid is between 10 and 20 per cent. neutralised. It has long been known that if either glycerol or mannitol be added to the solution undergoing titration the pink colour disappears until the alkali has been added in an equivalent quantity. Hildebrand (*J. Amer. Chem. Soc.*, 1913, 35, 860) followed the change in pH when varying amounts of mannitol were added to a boric acid solution. The curves A, B, C, D, E represent his observations. Curve E corresponds roughly to $K = 10^{-5}$, and thus the effect of the excess of mannitol was to magnify the K by about 10,000, and therefore boric acid can then be titrated to phenolphthalein. Similar curves were obtained by van Liempt (*Z. anorg. Chem.*, 1920, 111, 151), who also showed that glycerol and fructose produce analogous effects. The explanation probably lies in the

formation of a complex mannitol-boric acid, though Magnanini (*Z. physikal. Chem.*, 1890, **6**, 58) found that, although conductivity measurements gave evidence of some such combination in concentrated solutions, as soon as the boric acid solutions became dilute
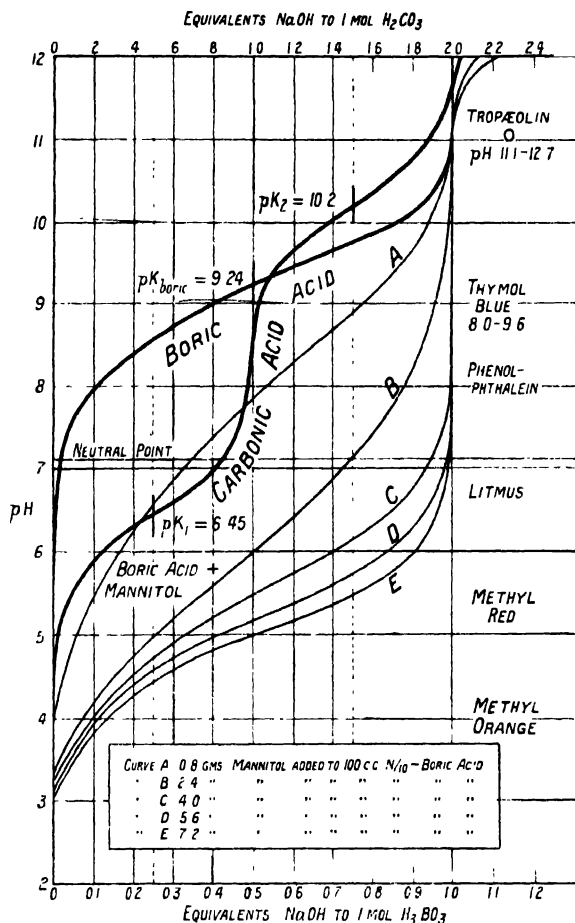
FIG. 153.—Neutralisation Curves of Carbonic Acid and Boric Acid in the presence of Mannitol.

the complex acid must have become hydrolysed for the conductivity measurements again became normal.   Fox and Gauge (*J. Chem. Soc.*, 1911, **99**, 1075) prepared a crystalline body, $C_6H_{15}O_nB$, from *alcoholic solutions*.   (For methods of determining boron compounds in foods and drugs involving the titration of mannitol-boric acid, see A. S. Dodd (

The carbonic acid neutralisation curve given in Fig. 153 shows the effect which any dissolved carbon dioxide will have on the accuracy of the boric acid estimation.

Baryta Vacuum Method of Estimating Carbon Dioxide.

This method depends upon the absorption of carbon dioxide by a saturated solution of baryta, neutralising the excess of barium hydroxide by bringing the solution to the phenolphthalein end-point, then adding an excess of a standard solution of an acid and returning to the methyl orange end-point with standard alkali. The curves given in Fig. 155 illustrate the principle upon which the method is based, for which the author is indebted to the late
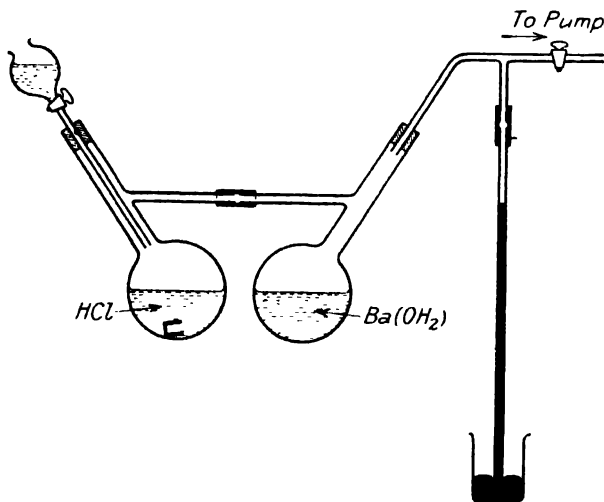
FIG. 154.—Apparatus for the Estimation of Carbon Dioxide.

Mr. F. J. Watson, M.A., M.Sc., of Melbourne, and also for the following particulars. The apparatus required is shown in Fig. 154. The carbonate sample is weighed out in a small glass capsule, which may be made from a test-tube, and is dropped into the distilling flask on the left. An excess of saturated barium hydroxide solution is put in the other flask. If the percentage of CO_2 in the sample is known approximately the necessary volume of $Ba(OH)_2$ to provide an excess is readily calculated. The system is then evacuated by the pump, which is preferably a Gaede, but may be a good jet pump. The system is isolated from the pump by the tap and the maintenance of the vacuum checked by the mercury gauge. Dilute HCl is cautiously admitted from the tap funnel and the flask on the right shaken to absorb the CO_2 as

evolved. The bottom of the first flask is now heated directly with a small Bunsen flame and the distillation continued vigorously for at least 5 minutes. The vacuum is now broken by opening the tap of the tap funnel, and the $Ba(OH)_2$, $BaCO_3$ mixture in the second is rapidly titrated with HCl to the phenolphthalein end-point. (If this end-point is over-shot return quickly with NaOH before any CO_2 is lost.) If the volume and normality of the original $Ba(OH)_2$ is known this titre will give a measure of the
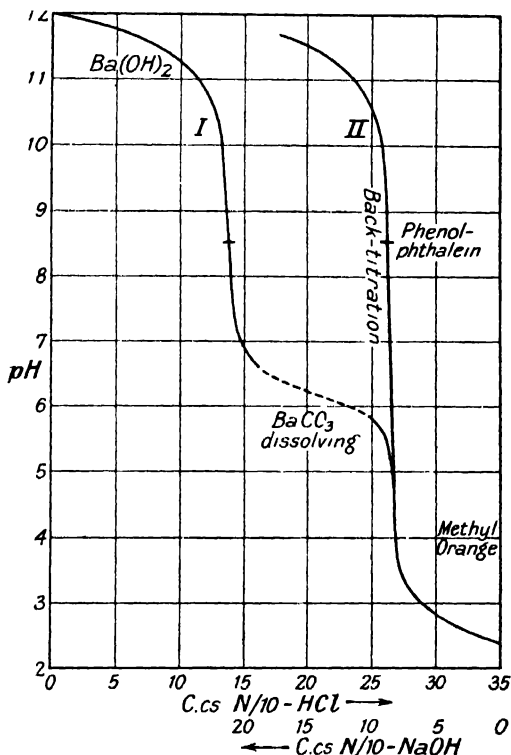
FIG. 155.—Principle of Estimating Carbon Dioxide.

CO_2 absorbed, but in most cases it is not used. A slight excess of the HCl over that required to dissolve the carbonate is now added, and the excess back-titrated with NaOH to the methyl orange end-point. It is not practicable to titrate the $BaCO_3$ directly, as its reaction with the acid is too slow where the excess of acid is very small in the vicinity of the end-point.

Curve I in Fig. 155 refers to the titration of a solution of

barium hydroxide containing suspended barium carbonate. The broken line gives the approximate course taken by the pH of the solution, exact values not being possible on account of the evolution of carbon dioxide which was taking place. The dissolution of the barium carbonate is indicated by a downward inflexion and may be detected with methyl orange, though preferably the exact end-point should be judged by comparison with the colour produced in solution buffered at about pH 4·5. Curve II is the back-titration curve with NaOH of a solution containing an excess of free acid after CO_2 has been expelled by boiling. As may be seen from the great inflexion thereby obtained, such a titration will lead to more satisfactory results.

According to Lindsey and Yoe (*Anal. Chem.*, 1949, **21**, 513) the baryta solution in contact with the barium carbonate precipitate may be titrated with oxalic acid to thymolphthalein (pH 8·7–9·2) without any risk of attacking the precipitate, which is possible when phenolphthalein is used. The pH of a saturated solution of barium carbonate is 8·8 at 20°.

Estimation of Carbon Dioxide in Gas Mixtures.

If a gas mixture containing carbon dioxide is passed through a solution of sodium bicarbonate some of the carbon dioxide will dissolve. Owing to the preponderance of bicarbonate ions and the small dissociation constant, K_1, of carbonic acid, Henry's Law will be obeyed and consequently, at a given temperature, the partial pressure, p_{CO_2}, of the carbon dioxide in the gaseous mixture compared with the concentration of dissolved carbon dioxide, $[H_2CO_3]$, will be fixed. Hence $p_{CO_2}/[H_2CO_3] = \lambda$ (a constant), and also

$$p\mathrm{H} = p\mathrm{K}_1 + \log_{10}\frac{f_{\pm \mathrm{NaHCO_3}}[\mathrm{NaHCO_3}]}{f_{\pm \mathrm{H_2CO_3}}[\mathrm{H_2CO_3}]}.$$

$f_{\pm \mathrm{H_2CO_3}}$ can be put equal to unity, without introducing any appreciable error and therefore, combining the two equations, it follows that

$$p\mathrm{H} = p\mathrm{K}_1 + \log_{10}f_{\pm \mathrm{NaHCO_3}} + \log_{10}[\mathrm{NaHCO_3}] + \log_{10}\lambda - \log_{10}p_{CO_2}.$$

If, however, it is desired to estimate the carbon dioxide in a sample of air at atmospheric pressure, the constant λ becomes equal to $760 \times 22\cdot4/\alpha_{CO_2}$, where α_{CO_2} is the solubility co-efficient of carbon dioxide at the particular temperature and is equal to

$$\frac{\text{g.-mols. of } CO_2 \text{ dissolved in 1 litre}}{\text{g.-mols. of } CO_2 \text{ present in 1 litre of air}}.$$

The percentage of carbon dioxide is $\dfrac{p_{CO_2} \times 100}{p_{atmos.}}$.

Hastings and Sendroy (*J. Biol. Chem.*, 1925, **65**, 445) put $pK_1 + \log_{10} f_{\pm NaHCO_3} = pK_1' = pK_1 - 0.5\sqrt{\mu}$, μ being equal to $\frac{1}{2}\Sigma cz^2$. Taking $\alpha_{CO_2} = 0.738$, the above equation becomes

$$pH = pK_1' + 1.362 - \log_{10} p_{CO_2}.$$

According to Hastings and Sendroy, $pK_1 = 6.33$, whereas Wilson, Orcutt and Peterson (*Ind. Eng. Chem., Anal. Edn.*, 1932, **4**, 357) give 6.31 at 26° C. Using 0.001 N-NaHCO$_3$ the expression simplifies to

$$pH = 7.67 - \log_{10} p_{CO_2}.$$

The latter workers state that if the pH values of the resulting NaHCO$_3$ + CO$_2$ solutions are determined with the glass electrode, the CO$_2$ estimations have an accuracy of 4 per cent.
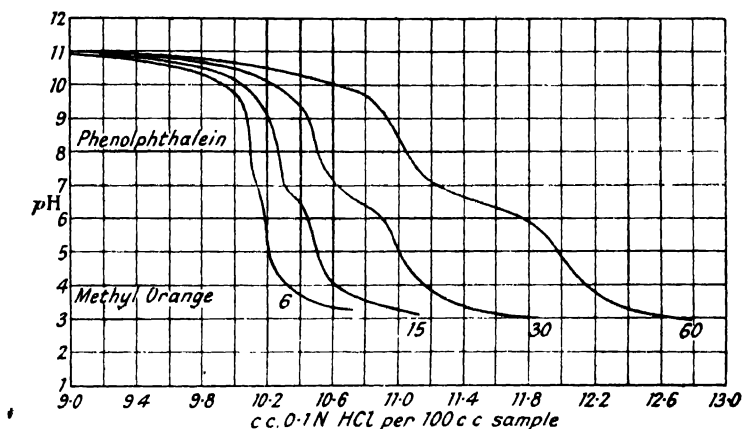
FIG. 156.—Titration Curves of Water containing 170 p.p.m. of Sodium Hydroxide and 6, 15, 30 and 60 p.p.m. CO₂. (Schroeder, 1933.)

Estimation of Carbonates in Boiler Waters.

Warder (*Chem. News*, 1881, **43**, 228) pointed out that alkali carbonates may be titrated with hydrochloric acid using phenolphthalein, but, as may be seen from the lack of sharpness in the inflexion of the carbonic acid neutralisation curve (Fig. 156) corresponding with the formation of sodium bicarbonate, it is necessary to titrate to the shade of phenolphthalein set up, with a given concentration of the indicator, at the pH at which the true end-point is actually reached. Owing to the possible loss of carbon dioxide during the titration Benedetti-Pichler, Cefola and

Waldman (*Ind. Eng. Chem.*, *Anal. Edn.*, 1939, **11**, 327) recommend the need for carrying out the titration in a closed system.

Another source of error in titrating to phenolphthalein (*i.e.*, to $NaHCO_3$) and then to methyl orange (H_2CO_3) occurs in extremely dilute solutions owing respectively to hydrolysis and to the ionisation of dissolved carbon dioxide assuming disturbing dimensions. This is brought out clearly in Fig. 156, obtained by Schroeder (*Ind. Eng. Chem.*, *Anal. Edn.*, 1933, **5**, 389), which gives the final inflexions of pH titration curves of dilute sodium hydroxide solutions of 6, 15, 30 and 60 parts per million of carbon dioxide. In no case does methyl orange indicate correct equivalence points, whereas phenolphthalein will lead to inaccuracy unless titration is carried out by matching with a solution of phenolphthalein adjusted to a suitable pH.

According to Fleisher (*Ind. Eng. Chem.*, *Anal. Edn.*, 1943, **15**, 742), the titratable alkalinity of boiler feed-water, which is of order $0.0003M.Na_2CO_3$, may be estimated by titrating with 0.033 $N.HCl$ to the purple grey colour of a screened indicator, made up of 0.55 gram of alphazurine and 0.45 gram of the sodium salt of methyl red per litre of water (3 drops per 100 c.c. of water). The first end-point is detected by means of phenolphthalein and the screened indicator is, of course, not added until this end-point has been passed.

Electrometric Titration of Barbiturates.

Krahl (*J. Physical Chem.*, 1940, **44**, 449) has determined the apparent dissociation constants at 25° C. of a considerable number of substituted barbituric acids at a concentration of 0.002 M. Expressed in terms of pK they range from 7.20 to 8.32. The pK of diethylbarbituric acid is 7.90. With increasing ionic strength, μ, to 2.00 caused by the inclusion of sodium chloride in the acid solution the apparent pK falls to 7.56. The members of this class of drug are available as the sodium salts under such names as Veronal, Amytal, Neonal, Nembutal.

Titration with hydrochloric acid of solutions of any of these sodium salts should therefore liberate the substituted barbituric acid between approximately pH 10 and pH 6, immediately after which rapid diminution in pH should occur owing to the presence of free hydrochloric acid. It follows therefore that these barbiturates can be titrated with hydrochloric acid to methyl red as advocated in the German and Swedish Pharmacopœias. The titrations may also be carried out with either the hydrogen, glass or quinhydrone electrodes (Tabern and Shelberg, *Ind. Eng. Chem.*, *Anal. Edn.*, 1931, **3**, 279).

Estimation of Pyridine Bases.

Considerable quantities of the vapours of pyridine, quinoline, isoquinoline and their homologues are found in the crude gas from by-product coke ovens. Whereas the higher boiling fractions contain bases which condense with the tar, the more volatile bases pass to the ammonia saturator where they form hydrosulphates and contaminate the ammonium sulphate. Rhodes and Younger (*Ind. Eng. Chem., Anal. Edn.*, 1933, **5**, 302) extract these bases, together with a little ammonia, from an alkaline solution with xylene. After destroying the ammonia with sodium hypobromite, the free organic bases are distilled into dilute hydrochloric acid which is then titrated electrometrically with alkali using the quinhydrone electrode ; inflexions being obtained marking the neutralisation of the excess hydrochloric acid and the liberation of the base from its hydrochloride.

Titrimetric Estimation of Acetaldehyde.

Acetaldehyde forms with sodium bisulphite in aqueous solutions the characteristic aldehyde bisulphite compound. This compound is so stable that at pH 2–3 none of the combined bisulphite is susceptible to the action of iodine and only the excess of sodium bisulphite can thus be titrated. Between pH 6–8, Tomoda (*J. Soc. Chem. Ind.*, 1929, **48**, 76T) has found that the decomposition of the bisulphite compound is inappreciable, but at about pH 8 sufficient dissociation occurs to enable all the combined bisulphite to be titrated with iodine. Above pH 9 the oxidation of the aldehyde by the iodine solution also becomes possible. By buffering the solution at pH 8 with a large excess of sodium bicarbonate the combined bisulphite can be titrated.

Titration of Sodium or Potassium Iodide.

A convenient method is to oxidise the iodide to iodate by passing bromine vapour through a sulphuric acid solution and then driving off the excess of bromine by boiling. On adding an excess of potassium iodide to the acid iodate solution, iodine is liberated which may be titrated with sodium thiosulphate. Sadusk and Ball (*Ind. Eng. Chem., Anal. Edn.*, 1933, **5**, 386) state that above pH 2 the reaction with thiosulphate is slow, whereas below pH 1 errors are introduced through air-oxidation of the iodine which might assume relatively large proportions when small amounts of iodine are to be estimated. In such cases the pH of the test-solution should be adjusted between pH 1 and pH 2.

Estimation of Iodate in the Presence of Bromate and Chlorate.

If a solution of potassium iodide be added to one containing IO_3', BrO_3' and ClO_3', which has previously been buffered between pH 4 and 5, only the iodate-ions will be reacted upon, thus:

$$IO_3' + 5I' + 6H^{\cdot} \rightarrow 3H_2O + 3I_2$$
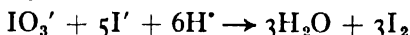
and the liberated iodine may be titrated with sodium thiosulphate (Kolthoff and Hume, *Ind. Eng. Chem., Anal. Edn.*, 1943, **15**, 174). After rendering the solution slightly acidic with either hydrochloric acid or sulphuric acid (*see* Britton and H. G. Britton, *J. Chem. Soc.*, 1952, 3887) the iodine, thereby liberated through the interaction of the bromic acid and the hydriodic acid, may then be titrated. According to Kolthoff (*Z. anal. Chem.*, 1921, **60**, 348), this reaction may be catalysed by the addition of a few drops of molybdate solution.

Micro-method of Estimating Sulphate.

Benzidine hydrochloride reacts with soluble sulphates to precipitate benzidine hydrosulphate which provides a method of detecting and estimating accurately small amounts of sulphate such as may be present in urine and in " soil-solutions." The method was introduced by Rosenheim and Drummond (*Biochem. J.*, 1914, **8**, 143) to estimate sulphate in urine. Before adding the precipitant they render the urine just acid to Congo Red, whilst Fiske (*J. Biol. Chem.*, 1921, **47**, 59) uses bromophenol blue and adds just sufficient alkali to turn the indicator yellow. By using either indicator the pH set up is approximately 3. Owen (*Biochem. J.*, 1936, **30**, 352) finds that the pH should be $2 \cdot 75 \pm 0 \cdot 3$ and Marsden and Pollard (*J. Soc. Chem. Ind.*, 1937, **56**, 464T) state that by using a benzidine hydrochloride solution containing 8 grams per litre the pH imparted to the solution is $2 \cdot 6 \cdot 2 \cdot 7$, and thus leads to quantitative precipitation.

Estimation of Ortho-, Pyro- and Meta-phosphoric Acids in Mixtures.

The three dissociation constants of orthophosphoric acid are so very different that it can be titrated to pH 4·5 giving NaH_2PO_4 and to pH 8·8 giving Na_2HPO_4. Pyrophosphoric acid in each of its first two stages of ionisation behaves as a fairly strong acid, $K_1 = 0 \cdot 14$, $K_2 = 1 \times 10^{-2}$ approx., whereas in its third and final stages it ionises as weak acids. Kolthoff (*Pharm. Weekblad*, 1920, **57**, 474) finds K_3 to be $7 \cdot 6 \times 10^{-7}$ and $K_4 = 4 \times 10^{-9}$. It follows that the pH curve of pyrophosphoric acid contains only

one well-defined inflexion, *viz.*, at *p*H 4–5 with 2 equivalents of alkali. Some doubt exists regarding the ionisation of meta-phosphoric acid, but there is reason to believe that neutralisation with a strong base is complete at about *p*H 5.

Now that anhydrous phosphoric acids are available commercially, the problem of their assay arises, especially as all three acids may be present together. The method of Gerber and Miles (*Ind. Eng. Chem., Anal. Edn.*, 1938, **10**, 519) consists of dissolving in ice-cold water in order to minimise hydration. Titrate with sodium hydroxide to *p*H 4, using bromocresol green, thereby forming NaH_2PO_4, $Na_2H_2P_2O_7$ and $NaPO_3$. A suitable amount of silver nitrate is added to reduce hydration and the titration is continued to *p*H 8·8, using thymol blue, to form Na_2HPO_4 and insoluble $Ag_4P_2O_7$. (N.B. $Na_4P_2O_7$ cannot be formed until about *p*H 11.) By adding an excess of silver nitrate not only will $AgPO_3$ and $Ag_4P_2O_7$ be precipitated, but also Ag_3PO_4, and this will release nitric acid, thus

$$Na_2HPO_4 + 3AgNO_3 \rightarrow Ag_3PO_4 + 2NaNO_3 + HNO_3,$$

which is titrated with alkali to methyl red.

Estimation of (*a*) Soluble Iodides and (*b*) Arsenious Oxide.

The reaction :

$$2H^{\cdot} + H_3AsO_4 \rightarrow HAsO_2 + 2H_2O + 2F$$

is governed by the expression

$$E = \varepsilon_0 - \frac{RT}{2F} \log \frac{[HAsO_2]}{[H_3AsO_4][H^{\cdot}]^2} \qquad . \qquad . \quad (i)$$

in which E is the effective oxidation potential and ε_0 the normal reduction potential, which according to Foerster and Pressprich (*Z. Elektrochem.*, 1927, **33**, 176) at 25° is equal to $+ 0·575$. (N-H = 0). In strongly acid solutions, they showed that the above equation holds true, from which it is seen that with increasing acid concentration E becomes more positive ; in other words, arsenic acid becomes more effective as an oxidising agent. Experimental values of E, (N-H = 0) obtained with solutions centimolar with respect both to arsenious and arsenic acids and having the concentrations of hydrochloric acid indicated, [HCl], are given below.

[HCl]	E.		[HCl]	E.
0·1 M.	+ 0·563		4·0 M.	+ 0·571
0·5 ,,	+ 0·539		6·0 ,,	+ 0·612
1·0 ,,	+ 0·536		8·0 ,,	+ 0·681
2·0 ,,	+ 0·545		9·4 ,,	+ 0·728

It will be observed that the potentials fall as the concentration of acid increases from 0·1 M. to 1 M. and thereafter rapidly increase. Arsenious acid is so very weak an acid that its ionisation in these acid solutions can be ignored, but this is not so with the primary ionisation of arsenic acid, except when the concentration of hydrochloric acid is sufficien. to repress the dissociation. This appears to be the case with concentrations of 1 M. and greater. In dilute acid solutions and in solutions in which the first stage of arsenic acid has been either partly or completely neutralised (in the latter case pH 4·8 is reached), the reaction becomes

$$3H^{\cdot} + H_2AsO_4' \rightarrow HAsO_2 + 2H_2O + 2F$$

for which

$$E = \varepsilon_0 - \frac{RT}{2F} \log \frac{[HAsO_2]}{[H_2AsO_4'][H^{\cdot}]^3} \qquad . \qquad \text{(ii)}$$

During the neutralisation of the second stage of arsenic acid, i.e., pH 4·8–pH 8·8, Na_2HAsO_4 is formed, producing $HAsO_4''$ ions. As the dissociation constant of arsenious acid is $10^{-9\cdot26}$, it follows that above pH 7·26, the concentration of arsenite ions cannot be neglected. However, from pH 4·8 to pH 7, the oxidation process involves some $HAsO_4''$ ions, thus

$$4H^{\cdot} + HAsO_4'' \rightarrow HAsO_2 + 2H_2O + 2F$$

giving

$$E = \varepsilon_0 - \frac{RT}{2F} \log \frac{[HAsO_2]}{[HAsO_4''].[H^{\cdot}]^4} \qquad . \qquad \text{(iii)}$$

As both ions, H_2AsO_4' and $HAsO_4''$, will then be present the effective oxidation potential will be determined by the two equations (ii) and (iii). The equations indicate the fundamental effect of the concentration of hydrogen ions on E. Thus if we assume that ε_0 has the same value for each of the three reactions, viz., + 0·575 volt, E becomes at pH 4·8, + 0·157 volt on the basis of (ii). With increasing pH, when expression (iii) becomes applicable E becomes considerably smaller.

The normal potential of the processes $I_2 \rightarrow 2I'$ and $I_3' \rightarrow 3I'$ is + 0·534 volt (N-H = 0). Comparing this potential with that of the arsenic system in fairly acid solutions, it will be seen that the latter voltages become increasingly larger as the acid concentration is increased. This means that in acid solutions arsenic acid behaves as an oxidising agent and therefore liberates iodine from iodides according to

$$2I' + H_3AsO_4 + 2H^{\cdot} \rightarrow HAsO_2 + I_2 + 2H_2O,$$
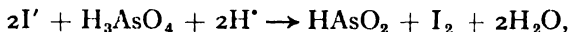
whereas at pH 4·8 and above, the potentials are in the reverse

order, and consequently iodine assumes the rôle of oxidising agent, thus

$$H_2O + I_2 + HAsO_2 \rightarrow 3H^\bullet + 2I' + H_2AsO_4'$$

and

$$H_2O + I_2 + HAsO_2 \rightarrow 4H^\bullet + 2I' + HAsO_4''.$$
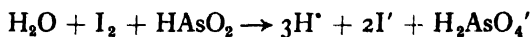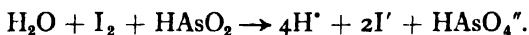
In actual fact, arsenious acid is completely oxidised between pH 4 and pH 9. Above this pH trisodium arsenate begins to form and owing to K_3 of arsenic acid being extremely small (*viz.*, $10^{-11\cdot53}$) the trisodium salt is considerably hydrolysed, with the result that, immediately after the oxidation of the arsenite has become complete, the iodine reacts with the free alkali to form a mixture of sodium iodate and sodium iodide.

Kolthoff (*Pharm. Weekblad*, 1919, **56**, 1322) showed that in the presence of hydrochloric acid of concentration not less than 4 N., arsenic acid is quantitatively reduced by hydriodic acid, and after a lapse of five minutes the liberated iodine can be titrated with sodium thiosulphate. In view of the potentials found by Foerster and Pressprich, it is obviously advantageous to employ as high a concentration of hydrochloric acid as possible in order to ensure complete oxidation of the iodide to iodine. The reaction has also been followed potentiometrically at 95° in 50 per cent. sulphuric acid solution by Robinson and Winter (*Ind. Eng. Chem.*, 1920, **12**, 775). Sodium iodide was the titrant.

Although pH 4–9 is a suitable range for the titration of arsenious acid with iodine, it is generally considered that pH 6·5 is most suitable. For ordinary work, it is sufficient to regulate the pH by introducing a small amount of sodium bicarbonate into the arsenite solution before titrating with iodine solution. This would establish a pH initially above 8, which would gradually fall owing to reaction with the hydriodic acid set free as the titration proceeds. To stabilise the pH between 6·5 and 7 the sodium bicarbonate may be saturated with carbon dioxide or else a buffer system consisting of molecular proportions of NaH_2PO_4 and Na_2HPO_4. A buffer system of boric acid and sodium borate has been recommended, but as $pK_{HBO_2} = 9\cdot24$ it would appear that it would set up too high a pH.

Similar considerations apply to the titration of antimonious oxide (in tartrate solution) with iodine.

Estimation of Saline Ammonia in Water.

The usual method is by the distillation of the water to which sodium carbonate has been added. This sets up too high a pH

which results in the hydrolysis of nitrogenous matter, *e.g.*, urea, gelatin, egg-albumen, peptone, casein, and so leads to high results. According to Nicholls and Foote (*Ind. Eng. Chem., Anal. Edn.*, 1931, **3**, 311) this may be avoided by buffering the solution to *p*H 7·4 by means of disodium hydrogen phosphate. The use of sodium carbonate for this purpose is not satisfactory, for as boiling proceeds *p*H variations occur ; if the *p*H falls below 7·4 the recovery of the ammonia will be incomplete.

Micro-detection of Silica.

Silica in solution can be detected and estimated colorimetrically by forming silico-molybdic acid which develops an intense characteristic yellow colour, preferably after heating for 5 minutes on a water-bath, at *p*H 1·2–2·0. Colorimetric comparison standards are prepared by treating varying amounts of sodium silicate with a 10 per cent. solution of ammonium molybdate (0·2 c.c. for each 5 mg. of SiO_2) and 5 drops of 50 per cent. sulphuric acid. The solutions are diluted to 100 c.c. and the colour allowed to develop to maximum intensity (10 minutes at 18°, or 5 minutes at 100° C.). The method is capable of estimating 1–50 mg. SiO_2 per litre (Alimarin and Sverev, *Mikrochem.*, 1937, **22**, 89 ; see also Schwartz, *Ind. Eng. Chem., Anal. Edn.*, 1934, **6**, 364).

Fluorescence Test for Molybdenum.

A fiery red fluorescence is produced when cochineal tincture is added to a molybdate solution and adjusted to *p*H 5·7–6·2. Many cations, however, interfere (Szebellédy and Jónás, *Mikrochem. Acta*, 1937, **1**, 46.)

Hydroxylamine and Hyponitrous Acid.

Both hydroxylamine and hyponitrous acid give colour reactions with a reagent consisting of resorcinol and potassium periodate. Rao and Rao (*Analyst*, 1938, **63**, 718) have shown that buffering with a mixture of 21·008 grams of citric acid and 200 c.c. of N-NaOH renders the tests most sensitive.

Chromatographic Separation of Amino-Acids.

Synthetic resins are now available commercially which have either : (1) the properties of bases of different strengths that are characteristic of the individual resins, or (2) the properties of acids of strengths that also are characteristic of the resins themselves. For this reason, basic resins may react with acids to extents which are dependent on the strengths of the bases and of the acids involved. Moreover, when a weak resin base

reacts with an acid it will only do so within definite *p*H limits. Similar remarks, of course, apply to the reaction of weak acid resins with bases. Strong base or strong acid resins, however, may react with very weak acids or bases respectively and, indeed, such reactions are facilitated by the fact that the neutralisations take place at solid-liquid interfaces and thus entail heterogeneous equilibria.

These resins are produced in the form of granular particles. They possess an open molecular structure due to cross-linking and lattice formation. Ion exchange resins are ionic solids in which one of the ionic species, either the anion or the cation, is a highly cross-linked, polymeric, non-diffusible ion of high molecular weight, the multivalent charge of which is balanced by charges of opposite sign on the diffusible ions. When, therefore, an acid, HA, or its ions, diffuses into a basic resin, ROH, in which the basic groups are located at various points within the lattice-structure and neutralisation ensues, thus

$$ROH + HA \rightarrow RA + H_2O \rightarrow R^{\cdot} + A' + H_2O$$
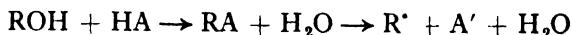
the anion, A′, will almost certainly be retained within the resin close to the R$^{\cdot}$ ion, *i.e.*, it will be adsorbed by the resin. Similarly an acid resin, RH, in neutralising a base, BOH, which has diffused into the resin,

$$RH + BOH \rightarrow RB + H_2O \rightarrow R' + B^{\cdot} + H_2O$$
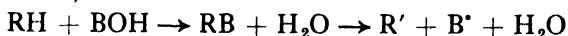
will most likely retain the B$^{\cdot}$ cations by adsorption.

The so-called base or cation exchange resins are therefore really acidic resins. They contain a multiplicity of centres, which may be either of the three general types : carboxylic, —COOH, phenolic, —OH, and sulphonic, —SO$_2$OH, at which the base exchange actually occurs. To produce these resins aromatic derivatives containing groups of the desired acidic strengths must be condensed with substances such as formaldehyde or benzaldehyde. Another method of preparing exchange resins, suitable for analytical work, makes use of resin in which polystyrene is cross-linked with divinylbenzene. To make a strongly acidic resin this resin is sulphonated, whereas to produce a resin which functions as a strong base the original resin is aminated to such an extent that quaternary amine groups are formed. (Kunin and Myers, *Ion Exchange Resins*, Wiley and Co., New York, 1950 ; Nachod, *Ion Exchange*, Academic Press, New York, 1949.)

Acid or anion exchange resins are basic resins and in their manufacture organic bases are introduced to confer on the resulting resins different strengths as bases, in fact a resin is now available which effectively neutralises the weakest acids, *viz.*,

silicic, boric and hydrosulphuric acids and phenol and, moreover, easily splits neutral salts (Amberlite IRA-400).

Freudenberg, Walch and Molter (*Naturwiss.*, 1942, **30**, 87) and Block (*Proc. S. Exp. Biol., Med.*, 1942, **51**, 252) used sulphonic acid type of cation exchangers to separate the basic amino-acids, arginine, histidine and lysine, and Cannan (*Ann. N. Y. Acad. Sci.*, 1946, **47**, 135) and Tiselius, Drake and Hagdahl (*Experimentia*, 1947, **3**, 15) have shown that glutamic and aspartic acid may be readily separated chromatographically by using an anion exchange column as an absorbent.

A study of Table 198 in which the pH ranges within which the acidic and basic groups of typical amino-acids react respectively with alkalis and strong acids, *i.e.*, from 1 to 99 per cent., will show at what pH values the amino-acid exists in solution respectively as an anion, A, and as a cation, C.

<div align="center">

TABLE 198

AMINO-ACID pH RANGES

</div>

Acid.	pK.	Reacts with		Ion A - Anion C - Cation.
		Alkali. pH range.	Strong Acid. pH range.	
Glutamic	pK_{a_2} 9·8	7·8–11·8		A″
	pK_{a_1} 4·2	2·2– 6·2		A′
	pK_b 11·9		4·2–0·2	C·
Aspartic	pK_{a_2} 9·9	7·9–11·9		A″
	pK_{a_1} 3·8	1·8 5·8		A′
	pK_b 11·9		4·2–0·2	C·
Histidine	pK_a 8·7	6·7–10·7		A′
	pK_{b_1} 8·2		7·9 3·9	C·
	pK_{b_2} 12·3		3·8 0·2	C··
Arginine	pK_a 14	12–16		A′
	pK_{b_1} 7		9–5	C·
	pK_{b_2} 11·7		4·4–0·4	C··
Lysine	pK_a 12	10–14		A′
	pK_{b_1} 7		9–5	C·
	pK_{b_2} 12		4·1–0·1	C··

It will be seen that in its first· stage of dissociation as an acid aspartic acid is slightly stronger than glutamic acid. Hence on passing a solution of the two acids down a column of a suitable anion-resin aspartate anions will be adsorbed more easily than those of glutamic acid.

Kunin (*Anal. Chem.*, 1949, **21**, 87 ; *Ind. Eng. Chem.*, 1949, **41**, 460) has described a scheme for the separation of the amino-

acids contained in protein hydrolysate in which amberlite IR-resins are used.   They are of the phenolic methylene sulphonic acid type and are base exchangers.   The following is an outline of the separation process.   •

TABLE 199

Protein Hydrolysate in HCl.

Amberlite IR-4B
(*a basic resin*)

HCl is adsorbed.   Amino-acids pass through.

Amberlite IR-4B
(*a basic resin*)

Glutamic and aspartic acids are   " Neutral " and basic acids pass
   adsorbed, *i e.*, as A'.   through.
Elute with Acetate Buffer.

Amberlite IR-50
buffered at pH 7·0
(*an acidic resin*)

Arginine and lysine are adsorbed,   Histidine and " Neutrals " pass
   i.e , as C'.   through.
Elute with HCl.

Amberlite IR-50
buffered at pH 4·7
(*an acidic resin*)

                                                          " Neutrals " pass
                                                             through.

Amberlite IR-4-400   Histidine is
(*a basic resin*)   adsorbed, *i.e.*,
                                      as C'.
                              Elute with HCl.

Lysine is   Arginine
 adsorbed,   passes
 i.e., as A'.   through.
Elute with
Acetate Buffer.

The data given in Table 198 and the acidic or basic nature of the resins employed account for the various separations. Thus at pH 7 the proportion of arginine and lysine existing in the form of monoacidic cati6ns, C˙, are approximately equal and are very much greater than that of histidine. Hence the arginine and lysine cations will preferentially be adsorbed. Furthermore Amberlite IRA-400 behaves as a very strong base and will therefore react with acids. As acids, lysine and arginine are extremely weak, but the pK$_a$ of lysine is 12 whereas that of arginine is 14 and consequently the former will be the first to react with the basic resin and to be adsorbed.

Some Analytical Uses of Exchange Resins.

Acidic resins have been used by Samuelson (*Svensk. Kem. Tidskr.*, 1940, **52**, 115 ; 1942, **54**, 124 ; *I.V.A.*, 1946, **17**, 5) to remove interfering cations from solutions before estimating (i) sulphate, (ii) phosphate, (iii) bromides, iodides and chlorates. Anions have similarly been removed by passing the solutions through columns of basic resins, *i.e.*, anion exchangers (Cohn, Parker and Tomkins, *Nucleonics*, 1948, **3**, 22).

Tap-water may be freed from cations and anions by passing it successively through a cation-exchange resin column and an anion-exchange resin column, or it may be passed through a column containing a mixture of the two types of ion-exchangers, the so-called " mixed bed " technique. In no case, however, is any un-ionised matter thereby removed. As far as its specific conductivity is concerned, *viz.*, 10^{-6}–10^{-7} mho, the purified water is superior to that obtained from several distillations in quartz vessels.

Carbonate-free sodium hydroxide may be prepared by passing a dilute caustic soda solution through a column packed with an anion-exchange resin.

Much work has been done to show the usefulness of acidic resins in the separation of the rare earths. If BX_3 represents a rare earth salt and HR the acidic resin, then

$$3HR + BX_3 \rightarrow BR_3 + 3HX.$$

Usually the solutions containing salts of the rare earths are adjusted to a pH value between 3 and 4 before they are passed through the cation-exchanger. The above reaction in proceeding to the right will cause the cation, B˙˙˙, to be adsorbed at the resin interface, and it will then be outside the sphere of action. When a number of rare earth cations are present in the solution the sequence of their adsorption by the resin will depend on such

factors as their ionic diameters, their hydration, valency, concentration and the relative basic strengths of their respective bases. It is on such factors as these that the facility with which the cations are able to penetrate into the internal structure of the resin and the magnitude of the forces which operate in adsorbing them must depend. Such differences do exist for these resins have been effective in separating the rare earths, and this is especially the case of the sequence in which the adsorbed cations may be removed from the resins by elution with suitable " complexing agents ", *e.g.*, citric acid. In this process the stability of the complexes that are also formed are of importance (*vide* Kunin,

CHAPTER XXXI

THE IMPORTANCE OF pH CONTROL IN THE DETECTION OF METALS WITH ORGANIC REAGENTS

THE efficiency of many of the newer methods of detecting and estimating metals in aqueous solution with organic reagents depends on the careful control of the hydrogen-ion concentration of the media and this is effected by the inclusion of suitable buffering systems. We shall now consider some of these reagents.

Dithizone (Diphenylthiocarbazone).

Fischer and Leopoldi (*Z. anal. Chem.*, 1934, **97**, 385) have shown that dithizone forms coloured complexes with many metals, which can be extracted from alkaline and sometimes from acid solutions with chloroform or carbon tetrachloride. It is possible to estimate the metal in the chloroform extract either colorimetrically or titrimetrically to the extent of 1 γ (*i.e.*, 0·001 mg.). Hibbard (*Ind. Eng. Chem., Anal. Edn.*, 1937, **9**, 127) suggests the use of the reagent to carry out separations by extracting the complexes formed within various pH ranges with chloroform. Thus the extract from solutions adjusted to pH 2 contains noble metals and mercury ; between pH 2 and 3, copper, bismuth, stannous ; pH 4–7, zinc, cadmium, lead and thallium, and all the foregoing which may have escaped extraction ; pH 7–10, all the above. (If this fraction is washed with 0·04 N-NH$_4$OH divalent tin is removed, then treated with KCN only lead, bismuth and thallium will remain if they have not, of course, already been removed) ; above pH 11, zinc will be extracted, cadmium alone remaining.

and molybdenum when present singly in aqueous solution as salts. The precipitations were carried out with a 2 per cent. solution of oxine in N-acetic acid in the presence of suitable buffer agents, boiling being carried out for 3–5 minutes. Thus copper is precipitated at *p*H 3–4 ; cobalt and nickel at *p*H 4 ; zinc at about *p*H 4·3 ; magnesium, *p*H 7–9 ; molybdenum at *p*H 3·2. Molybdenum redissolves at *p*H 7·7 and zinc at *p*H 14. Moyer and Remington (*Ind. Eng. Chem., Anal. Edn.*, 1938, 10, 212), however, found that when two metals are present the possibility of their separation is not entirely in accord with the conclusions arrived at by Fleck and Ward owing to co-precipitation when an excess of 20 per cent. of precipitant was employed. They showed that zinc can be separated from magnesium by maintaining the solution between *p*H 4·6–5·5 when the 8-hydroxy-quinoline precipitates the zinc complex. Zinc precipitates mainly at a lower *p*H, *viz.*, at 3·5, whilst magnesium precipitates within the range, *p*H 5·5–9.

Minute amounts of gallium can be detected by adding 8-hy-droxyquinoline to a solution at *p*H 2·6–3, shaking with chloroform and observing the fluorescence of the chloroform layer in U.V. radiation (Sandell, *Ind. Eng. Chem., Anal. Edn.*, 1941, 13, 844).

5-Nitroquinaldic Acid.

Lott (*Ind. Eng. Chem., Anal. Edn.*, 1938, 10, 335) has devised a colorimetric micro-method for the estimation of zinc. The solution is buffered between *p*H 2·5 and 8·0 with a mixture of ammonia and acetic acid. Precipitation with 5-nitroquinaldic acid is complete after digestion with excess of the precipitant for half an hour.

s-Diphenylcarbazide.

This is an exceedingly sensitive reagent for mercuric ions, but chloride ions must be absent and the concentration of electrolytes must be less than 0·003 N. With mercuric ions *s*-diphenyl-carbazide produces a purple coloration, but its shade is greatly influenced by the *p*H of the solution, which according to Laird and Smith (*Ind. Eng. Chem., Anal. Edn.*, 1938, 10, 576) should be adjusted to *p*H 3·5–4·5 for quantitative work, and for colorimetric comparisons the *p*H of the solutions should be kept at a constant value within this range at least to 0·3 *p*H unit. About *p*H 7 diphenylcarbazide functions as a *p*H indicator when the colourless solution assumes an orange hue.

7-Iodo-8-hydroxyquinoline-5-sulphonic Acid (" Ferron ").

Ferron is an extremely sensitive reagent for ferric ions by imparting to the solution a green to greenish blue colour, which, however, is appreciably affe¢ted by pH changes. The change in colour is less pronounced between pH 2 and 3, but even then it is great enough to require holding the pH to within o·2 pH to avoid errors greater than 2 per cent. in colorimetric estimations. Phthalate, glycine and acetate buffers are satisfactory for stabilising the pH, but citrate or phosphate buffers interfere. It should be mentioned that ferron behaves as a hydrogen ion indicator below pH 7, giving the solution a yellow or orange hue which gradually decreases with decreasing pH (Yoe, *J. Amer. Chem. Soc.*, 1932, **54**, 4139).

Ammonium aurine tricarboxylate (" Aluminon ").

Aluminium hydroxide when precipitated at a pH which corresponds with its maximum insolubility, *viz.*, at about pH 7, forms a bright red lake with aluminon. Winter, Thrum and Bird (*J. Amer. Chem. Soc.*, 1929, **51**, 2721 ; Winter and Bird, *ibid.*, 2964) do not allow the pH to exceed 7·3, whilst Roller (*J. Amer. Chem. Soc.*, 1933, **55**, 2437) prefers buffering at pH 6·3 with ammonium acetate and hydrochloric acid when they consider that greater sensitivity is obtained.

Dithio-oxamide (Rubeanic Acid).

This precipitates copper as a black precipitate when a solution of the reagent in 5 N-acetic acid is added to solution of a copper salt. By adjusting the pH to 3·5 with sodium acetate and acetic acid rubeanic acid precipitates nickel and cobalt as purple and black compounds respectively (Allport and Skrimshire, *Quart. J. Pharm. and Pharmacol.*, 1932, **5**, 461).

*   *   *   *   *

Brief reference will be made to three other organic reagents in the use of which the regulation of pH is advantageous.

Diphenylcarbazone, in alcohol, is sometimes used as a test for mercury in producing a violet or blue colour, although deep colours are given by Pb, Cu, Sn, Cd, Ni and Co. To obtain the best indication the test-solution must be adjusted to pH 7–8.

In acetic acid solution, salicylaldoxime produces a white precipitate or merely a turbidity with copper ions, but if the pH is fixed between 7 and 8 a green flocculent precipitate is obtained.

Sodium dihydroxytartrate osazone precipitates the calcium salt from solutions above pH 4—below that pH the osazone of dihydroxytartaric acid is precipitated. Another point is the possible interference of ammonium ions with the precipitation of

the calcium salt. This can be minimised by bringing the *p*H to 13 with sodium hydroxide before adding the reagent.

Extraction of Organo-metallic Complexes from Aqueous Solution by means of Organic Solvents.

In aqueous solution metallic ions enter into complex formation with organic reagents, such as dithizone, 8-hydroxyquinoline, salicylaldoxime, anthranilic acid and dimethylglyoxime. Many of these complexes impart characteristic colorations to their solutions which make possible the estimation of their concentrations by means of the spectrophotometer. Organic solvents are known, which are immiscible with the aqueous solutions, and in which both the " complexing agent " and the metallic complex are more soluble than in the aqueous solution. Furthermore, the conditions under which the metallic complex may be extracted, either partially or completely, involve *inter alia* the dissociation constant of the complexing agent, the instability constant of the complex itself and the *p*H of the aqueous solution.

To take the simplest case, we shall assume that the " complexing " agent is a monobasic acid, *e.g.*, dithizone, and represent it by HL, L' being the ligand, *viz.*, the actual " complexing agent ",

$$HL \rightleftharpoons H^{\cdot} + L'$$

for which the " apparent " or Brønsted dissociation constant

$$K_a = \frac{a_{H^{\cdot}} \times [L']}{[HL]}.$$

If the metallic complex is ML_n, which is formed by the interaction of $M^{\cdots n}$ and L' ions,

thus $$M^{\cdots n} + nL' \rightleftharpoons ML_n,$$

its instability constant in *aqueous solution*,

$$K_i = \frac{[M^{\cdots n}][L']^n_w}{[ML_n]_w}.$$

When an organic solvent is brought into contact with the aqueous solution and equilibrium is reached by sufficient shaking, the equilibria shown below will ensue.

Water Layer $H^{\cdot} + L' \rightleftharpoons HL$

$M^{\cdots n} + nL' \rightleftharpoons$ ML_n
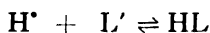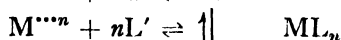
Interface

Organic Solvent Layer   HL ML_n
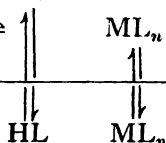
The equilibria across the interface may be represented by the respective partition coefficients, *viz.*,

$$p_c^{\,\bullet} = \frac{[ML_n]_w}{[ML_n]_o}$$

and

$$p_L = \frac{[HL]_w}{[HL]_o},$$

the subscripts w and o referring to *water* and *organic solvent*. If it be assumed that neither $M^{\cdots n}$, $H^{\bullet}$ nor L' ions are extracted by the organic solvent, then the *True Extractability*,

$$E_t = \frac{[\text{Metal as Complex in the Organic Solvent Phase}]}{[\text{Metal in all forms in the Aqueous Phase}]}$$

$$= \frac{[ML_n]_o}{[M^{\cdots n}]_w + [ML_n]_w}$$

$$= \frac{1}{\dfrac{p_c . K_i \, (a_H \cdot)_w^n}{p_L^n . K_a^n \, [HL]_o} + p_c}$$

If we set

$$\frac{p_L^n . K_a^n}{p_c . K_i} = K,$$

we get

$$E_t = \frac{1}{\dfrac{(a_H \cdot)_w^n}{K . [HL]_o^n} + p_c}$$

Should p_c be negligible, compared with the term $\dfrac{(a_H \cdot)_w^n}{K . [HL]_o^n}$, then the

Approximate Extractability, $E_a = \dfrac{K . [HR]_o}{(a_H \cdot)_w^n}$, whence the

True Extractability, $E_t = \dfrac{E_a}{1 + p_c . E_a}$.

Irving and Williams (*J. Chem. Soc.*, 1949, 1841) have calculated the magnitudes of the errors introduced by the neglect of p_c, when its value is between 0·1 and 0·001.

It will be seen that when p_c is of the order of 0·01–0·001, the error involved is similar to that of the experimental error and may be neglected.

TABLE 200

ERRORS CAUSED BY NEGLECT OF p_c

Percentage of Extraction assumed to be	E_a	Actual Percentage of Extraction calculated for		
		$p_c = 0\cdot1$	$p_c = 0\cdot01$	$p_c = 0\cdot001$
100	∞	90·9	99·0	99·9
99	99	90·1	98·0	98·9
90	9	82·6	89·2	89·9
50	1	47·6	49·75	49·8

Taking logarithms of the E_a equation,

we get $\qquad \log_{10}E = \log_{10}K + n(p\mathrm{H} + log_{10}[\mathrm{HL}]_o)$

and by defining $p\mathrm{H}_{\frac{1}{2}}$ as the pH value at which, *for the same concentration of HL in excess*, the extraction becomes 50 per cent., *i.e.*, $E = 1$, it follows that

$$\log_{10}1 = 0 = n(p\mathrm{H}_{\frac{1}{2}} + \log_{10}[\mathrm{HL}]_o),$$

whence by subtraction,

we get $n(p\mathrm{H}_{\frac{1}{2}} - p\mathrm{H}) = n\Delta p\mathrm{H} = -\log_{10}E = \log_{10}\dfrac{1-x}{x}$

where x is the percentage of the metal, which has passed as ML_n into the organic solvent layer.

Hence

$$x = 50\{1 - \tanh(1\cdot513n\Delta p\mathrm{H})\}$$

and $\qquad \dfrac{dx}{dp\mathrm{H}} = 57\cdot57n\{1 - \tanh^2(1\cdot513\Delta p\mathrm{H})\},$

so that when $x = 50$ per cent. and $\Delta p\mathrm{H} = 0$, i.e., at $p\mathrm{H}_{\frac{1}{2}}$,

$$\dfrac{dx}{dp\mathrm{H}} = 57\cdot57n \text{ per cent.}$$

This value has been verified by Irving and Williams in the case of zinc and dithizone.

The effect of valency, n, on the extractability, E, can be ascertained from the equation

$$E = \dfrac{K.[\mathrm{HL}]_o}{(a_{\mathrm{H}})_w^n},$$

and according to Irving and Williams an increase of 1 unit in the pH value of the solution being extracted will increase the extractability by 10 times when $n = 1$, by 100 times when $n = 2$, and by 1000 times when $n = 3$.

Hence the extractability at any pH value depends on $pH_{\frac{1}{2}}$ and the concentration of $[HL]_o$ actually present in the organic solution layer.

Irving, Cooke, Woodger and Williams (*ibid.*, 1847) find that as organic solvents carbon tetrachloride, monochlorobenzene or chloroform may be used in conjunction with dithizone.

Curves I, II and III in Fig. 157 were drawn by Irving and Williams to show the dependence of the percentage of complex extracted by the organic solvent on the magnitude of K, the concentration, $[HL]_o$, of the " complexing agent " in the organic solvent and the pH of the aqueous solution. For each curve, K was assumed to be 10^4. Curve I is based on the assumption
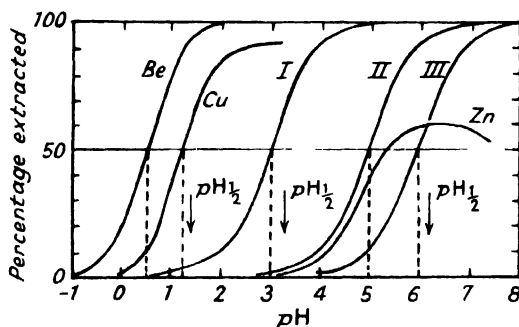
FIG. 157.—Extraction—pH Curves.

that $[HL]_o$ is 10^{-5}, curve II, 10^{-7}, and curve III, 10^{-8} mols per litre. They point out that the curves could equally well represent systems with $K = 10^6$, 10^2 and 1 respectively of three different bivalent metals in which $[HL]_o$ is equal to 10^{-6} mol/litre. These curves show how a knowledge of the mutual disposition of such curves, or, of the three parameters, $pH_{\frac{1}{2}}$, K and $[HL]_o$, is an " invaluable prerequisite to any reasoned attempt at separation." The dotted vertical lines to the points corresponding to 50 per cent. extraction on curves I, II and III indicate the values of $pH_{\frac{1}{2}}$ for the particular concentration of reagent, $[HL]_o$.

Furman, Mason and Pekola (*Anal. Chem.*, 1949, **21**, 1325) have found that the cupferrates of tervalent iron and titanium, sexavalent molybdenum and quinquevalent vanadium may be extracted with chloroform in quantities ranging from a microgram to a milligram. Melnick, Freiser and Beeghly (*Anal. Chem.*, 1953, **25**, 856) used tributylphosphate to extract ferric thiocyanate, formed by the addition of 3 mols of sodium thiocyanate per mol of ferric salt, from aqueous solution and found that 55 per cent. of the iron was extracted at pH 0·25, 81 per cent. at pH 1·0 and

95 per cent. at *p*H 2·10. The fact that ferric thiocyanate can be so extracted cannot be ascribed to hydrothiocyanic acid being a weak acid, for Gorman and Connell (*J. Amer. Chem. Soc.*, 1947, **69**, 2063) have shown it to be quite as strong as perchloric acid.

Acetylacetone has been used by Steinbach and Freiser (*Anal. Chem.*, 1953, **25**, 881) in the dual role of complexing agent with beryllium, copper and zinc and as the organic solvent of the metallic chelates originally formed in the aqueous media. This is possible, for acetylacetone is soluble in water to an extent of 17 gms. per 100 c.c. Advantages accruing from the use of acetylacetone as the extracting solvent are (i) the concentration, $[HL]_o$, is of course fixed, (ii) metal acetylacetonates are likely to be very much more soluble in acetylacetone than in water, (iii) the high concentration, $[HL]_o$, should enable it to be carried out from solutions of low *p*H with the possible consequence that the high concentration of acid should prevent the hydrolysis of the complex acetylacetonates.

Curves, marked Be, Cu and Zn, illustrate the effect of *p*H on the amounts of the respective complexes extracted by the acetylacetone. The $pH_{\frac{1}{2}}$ value for beryllium is 0·67, for copper 1·10, and for zinc 5·10. As may be inferred from the foregoing mathematical considerations, the concentration of metal present in the original aqueous solution is without effect on the shape and the position, with respect to the *p*H axis, of the extraction curve. This is borne out by the fact that Steinbach and Freiser used 100, 1000 and 2500 micrograms of copper for the distribution between 10 c.c. of the two phases and the points obtained all fell on the same curve.

In neither case, however, did the extraction reach 100 per cent. For beryllium it reached 97·5 per cent., for copper 87·3 per cent. and for zinc just over 60 per cent. The authors consider that the reason why neither beryllium nor copper could be completely extracted even though *p*H values were high enough theoretically was that the minimum ratio of the distribution of their complexes between solvent and water had been reached. In the case of zinc, hydrolysis of the zinc acetylacetone apparently occurred before a constant p_o was reached, no doubt due to hydrolysis caused by the high *p*H value of the aqueous layer.

For further information the reader is referred to Irving and Williams, *Analyst*, 1952, **77**, 813 ; Freiser, *ibid.*, 830 ; McCurdy and G. F. Smith, *ibid.*, 846 ; Cabell, *ibid.*, 859.

CHAPTER XXXII

THE IMPORTANCE OF HYDROGEN-ION CONCENTRATION IN THE ELECTRO-DEPOSITION OF METALS

BEFORE discussing the necessity for the careful regulation of the hydrogen-ion concentration of solutions from which certain base metals, such as nickel, cobalt, iron, and manganese, are to be cathodically deposited, it will be an advantage to consider the essential factors on which electrode deposition depends. They are as follow : (1) the relative position of the metal in the electrochemical series, *i.e.*, its normal electrode potential, and the effect which variations in metal-ion concentration will have upon the actual metal potential set up during deposition, (2) the potential of the hydrogen electrode when immersed in the particular solution (3) the polarisation produced at the cathode, (4) the hydrogen over-voltage or over-potential, (5) current density ; and (6) the precipitation pH of the hydroxide.

It should not be forgotten that the order in which the metals appear in the Electropotential Series (Fig. 159) is purely relative, and that the signs, positive and negative, refer only to the potentials in terms of the arbitrary potential standard, *viz.*, the assumption, which is certainly not true, being made that the potential of the Normal Hydrogen Electrode is zero. On this basis, the variations in the reversible potentials, introduced by differences in concentration, c, of the respective ions in the electrolyte is given by

$$E = \varepsilon + \frac{RT}{nF} \log_e c$$

(see p. 13, Vol. I).

The metals are deposited on the negative pole, the cathode. If, for the moment, it is assumed that metals are deposited at their respective reversible potentials, then during the electrolysis of a solution containing different cations, the most noble metals will deposit at the least negative potentials and hydrogen will not be evolved, nor will the baser metals be deposited until the cathode has acquired the appropriate, more negative potentials. The precise potentials of the cathode throughout electrolysis can be measured in terms of that of the arbitrary hydrogen standard, merely by measuring the potential difference between the cathode

and a standard calomel electrode with the capillary of the electrode pressing lightly but not too tightly against the cathode.

In actual practice, only the more noble metals deposit at potentials close to their reversible potentials. Polarisation occurs, the extent of which depends on the current density (*i.e.*, the current per unit area of the cathode) and also on the temperature. The result is that deposition does not occur until the cathode has reached a somewhat more negative potential. This excess in negative potential for noble metals is usually of the order of a few centivolts only. The metals baser than hydrogen, *i.e.*, more negative, *e.g.*, iron, nickel, cobalt, chromium, and manganese, require considerable polarisation before they can be deposited, and therefore on electrolysis, potentials are required for the cathodic deposition of these metals which are considerably more negative than the calculated equilibrium potentials.

The proximity of the cathode potential to that which would be assumed by a hydrogen electrode immersed in the electrolyte, supposing it to behave normally, is a matter of some great importance, for on it depends whether metal, or hydrogen, or both will be discharged at the cathode.

In determining the potential of the hydrogen electrode, it is necessary to introduce platinised platinum which serves as a catalyst in the equilibria :

$$H_2 \rightleftharpoons 2H \rightleftharpoons 2H^{\cdot},$$
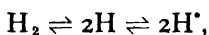
so much so that the equilibria appear to be spontaneously reversible. In electrolysis using a platinised platinum cathode hydrogen gas is evolved at the reversible potential. In general, however, hydrogen is evolved at the surfaces of other metals when used as cathodes, and also when they have already become covered with some metal deposited from the solution. Under these conditions, the cathode potential at which hydrogen begins to be liberated is more negative than the reversible potential,

viz., at
$$E_H = -\frac{RT}{F} \times 2{\cdot}3026 \times pH$$
$$= -0{\cdot}058 \; pH \text{ at } 18°. \cdot$$

The difference between the potential given by this expression and the potential at which hydrogen actually begins to be evolved is the so-called *hydrogen overvoltage* or *hydrogen overpotential*. It depends on (i) the surface and angle of inclination of the cathode, (ii) the temperature, (iii) the current density. With zinc this hydrogen overvoltage is so great that it is sufficient to prevent the production of hydrogen from acid solutions of zinc salts,

despite the fact that the normal electrode potential of zinc is as much as 0·7 volt more negative than that of hydrogen. In such solutions, however, it is essential to keep the polarisation of the zinc cathode as low as possible, and consequently, relatively small current densities must be used which incidentally restrict the use of the bath as regards its " throwing power," *i.e.*, the even distribution of the deposited metal on the electrode, an essential factor in zinc-plating.
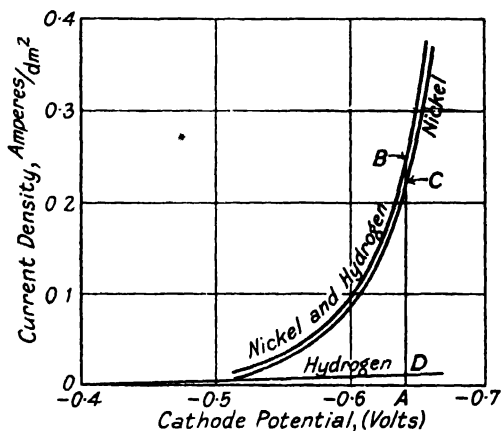
FIG. 158.—Variation in Cathode Potential with Current Density.

Referring to the base metals, it is found that the great electronegativeness of magnesium is such that whenever a potential is applied to a cathode in a magnesium salt solution, the current is utilised in discharging hydrogen, thereby depleting the catholyte of its hydrogen ions and consequently magnesium hydroxide eventually begins to precipitate. This prevents the attainment of the requisite magnesium potential. The reason will be apparent from the chart, Fig. 159, which gives the hydrogen electrode potentials for different pH's side by side with the electrolytic potentials of the various metals. The stages at which the various hydroxides begin to be precipitated are also indicated. The gradually increasing concentration of hydroxyl ions brought about by the evolution of hydrogen in the liquid surrounding the cathode will, though the conditions may also prevail for the metal to be deposited on the cathode, approach that pH when the hydroxide or basic salt begins to form. This may make the deposited metal incoherent and spongy through the hydroxide becoming embedded in the crystal structure of the metal, thereby imparting to it a dull dark surface. As this type of deposit often follows the vigorous discharge of

hydrogen the sponginess has been attributed solely to the action of the hydrogen in preventing the normal growth of the metallic crystals. In the case of nickel and cobalt deposition, however, a certain amount of basic salt deposited within the deposits has been found to have a beneficial effect in leading to the production of harder deposits (see p. 235). Gas evolution does occasionally impair the deposit, giving it an uneven and sometimes streaky appearance, but it is not in itself the real cause of the incoherence of the deposits. The use of dilute solutions and the too rapid passage of the electricity through the solution, by employing large currents compared with the area of the cathode, are conducive to the evolution of hydrogen instead of the liberation of metal at the cathode. Thus Patterson (*Proc. Univ. Durham Phil. Soc.*, 1912, **4**, 187) has shown that there are conditions under which solutions of salts of iron, nickel, cobalt, zinc, cadmium or manganese can be electrolysed to produce nothing but hydrogen and the respective hydroxides at the cathodes. Much of the hydroxide (or basic salt) though set free from the catholyte can in some cases be prevented from contaminating the deposited metal by either agitating the solution or employing a rotating cathode. Wherever possible electrolytes should be as concentrated as possible and kept slightly acid. This, however, is not always possible, as will be seen to be the case with certain base metals, yet zinc in spite of its " baseness " can, under suitable conditions, be deposited from either solutions containing
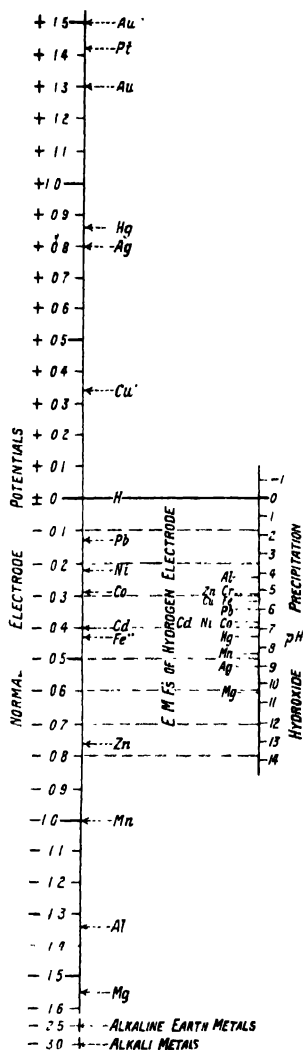
Fig. 159.—Relationship between Normal Electrode Potentials of Metals and Potentials of the Hydrogen Electrode at which their hydroxides begin to be precipitated.

free acid or solutions in which *concentration of the acid is immeasurably small, as far as chemical methods are concerned, but which nevertheless is great enough to affect deposition and requires careful control to prevent the simultaneous deposition of zinc hydroxide with the zinc.* Another point should be borne in mind in regard to the effect which current density may have on the nature of the deposit. In general, when a metal can be so deposited a low current density favours the formation of a coarse crystalline non-adherent deposit, the low current density lowering the cathode potential slightly below that corresponding to equilibrium conditions ; but the application of a high current density necessitates a higher cathodic polarisation E.M.F. before deposition can ensue and the greater rate at which deposition can then take place produces a smooth coherent metal composed of fine crystals. The simultaneous liberation of hydrogen with the metal in the case of metals like iron, nickel, and manganese results in the absorption by the deposited metals of some hydrogen which makes them brittle and causes them to have a tendency to peel off and to crack. The hydrogen can be readily driven off by heating.

It is in the electro-deposition of base metals where the very small concentrations of hydrogen ions make or mar the efficiency of a process. This will be inferred from the proximity of their normal electrode potentials to those potentials which a hydrogen electrode if it were immersed in the solutions would assume when about to precipitate the various hydroxides. (See Fig. 159.) Thus, if base metals, such as cobalt, nickel, cadmium, and iron, could be deposited reversibly, *i.e.*, at the equilibrium potentials, from their salt solutions, containing, say, 1 gram-molecule of the respective cations per litre, then it will be seen from Fig. 159 that these potentials are so close to the theoretical potentials required for the reversible discharge of hydrogen and the resulting precipitation of the hydroxide or basic salt, that electrolyses could only be carried out in which varying amounts of current would be wasted in liberating hydrogen, not to mention the deleterious effect which the basic precipitates may have in becoming entangled in the metallic deposits. These precipitations can, however, be avoided by including in the bath certain buffering agents or mixtures which will keep the pH below that required for the precipitation of the hydroxide, no matter how much hydrogen may be discharged from the catholyte.

The base metals are irreversible and require high polarisations for their deposition, which increase with increasing current density. The discharge of hydrogen at their surfaces is governed

by the magnitudes of the hydrogen overvoltage under the conditions existing during the electrolyses.

The hydrogen over-voltage for metals of the iron group is at ordinary current densities usually low. As may be seen from Fig. 158, the reversible potential of nickel in a salt solution containing 1 gram-molecule of its ions is less negative than the reversible potential of hydrogen at the *p*H, 5–6, of ordinary nickel salt solutions, yet nickel deposition is always accompanied by hydrogen evolution even at small current densities. This is due to the nickel cathode becoming polarised, no doubt through the cathode becoming a nickel-hydrogen alloy, the potential of which becomes increasingly negative, when either the hydrogen-ion concentration of the solution or the current density is raised (Foerster and Schade, *Z. Elektrochem.*, 1916, **22**, 96). Foerster (*Elektrochemie wässriger Lösungen*, 1922, p. 366) states that for the deposition of nickel from a solution, normal with respect to nickel sulphate and one-hundredth normal with respect to sulphuric acid, with 0·9 ampères per square decimetre the cathode efficiency was as low as 40 per cent. at 16° C., *i.e.*, 60 per cent. of the current was utilised in the generation of hydrogen, whereas the diminution in the polarisation produced by raising the temperature to 50° C. gave an enhanced efficiency of 80 per cent. That hydrogen has a marked effect on the potential of a base metal may be seen from an observation of Smits and Lobry de Bruyn (*Theory of Allotropy*, 1922, p. 327), who found that the potential of nickel free from hydrogen in N-NiSO₄ was − 0·194 volt, but changed with time to − 0·35 volt, the potential of the hydrogen electrode in the solution.

In order to deposit base metals from their solutions, it is necessary to employ concentrated metallic salt solutions, to keep the cathode potential at which deposition takes place as slightly negative as possible and to keep the *p*H of the solution only just below that at which the hydroxide becomes precipitable. This, as may be seen from Fig. 158, will tend to make the hydrogen potential more negative than that of the metal, and coupled with the small hydrogen over-voltage, will enable the metal to be deposited. The differences between the metal- and hydrogen-potentials which generally are small, will cause some hydrogen to be liberated. Its proportion may be considerably reduced by employing a high current density which will also increase the rate of deposition. Another important factor is the maintenance of as large a ratio of the concentrations of metal ions to hydrogen ions as possible. The upper curve, given in Fig. 158 (*vide* Haring, *Trans. Amer. Electrochem. Soc.*, 1924, **46**, 110) is typical of the effect produced

on the cathode potential by increasing the current density of a
nickel plating solution (cathode potentials are measured by joining
a calomel half-element in direct contact with the cathode and
finding the fall in potential between the two poles in the usual way).

It is seen that nickel did not begin to deposit until the potential
of the cathode became more negative than -0.5 volt (N.H $= 0$),
hydrogen alone being liberated. Thereupon a rapid increase in
potential occurred with the increasing current density. This
enabled more and more nickel to be deposited and prevented
relatively less and less current being wasted in liberating hydrogen.
The curves C and D, which were plotted from the various current
efficiencies at the respective current densities and cathode poten-
tials, show what portions of the current densities were utilised in
depositing nickel and evolving hydrogen respectively. As the
cathode efficiency is the ratio of the metal actually deposited
to that which the current would have deposited under ideal
conditions, i.e., if no current had been dissipated in producing
hydrogen, it will be seen from Fig. 158 that for any particular
point, B, say, on the upper curve, the amount of current repre-
sented by the ordinate AD was utilised in setting hydrogen free,
and that shown by AC the amount used in metal deposition.
The total current (in terms of current density) passed then was
equal to AD $+$ AC $=$ AB, and therefore the percentage nickel
cathode efficiency was AC/AB $\times$ 100. Hence if curves similar
to those given in Fig. 158 have once been ascertained for any given
electrolysis bath under given conditions the measurement of the
cathode discharge potential will constitute a method by which the
cathode efficiency can be calculated. As emphasised by Haring,
the latter is a most important factor in determining the " throwing
power " of nickel plating baths, in other words, in obtaining
baths, which will cause the nickel to be deposited uniformly over
the article undergoing plating.

Much of the efficiency depends upon keeping the hydrogen-ion
concentration of the bath as low as possible without producing
deposits contaminated with basic precipitates. The hydrogen-ion
concentration of an electrolysis bath as a whole, depends primarily
upon securing equal anode and cathode efficiencies, for if the
former becomes less than the latter, the solution will become more
acid, and *vice versa*. If the acidity of the bath increases, there will
be a tendency for the anode to corrode, and thereby to lower the
cathode efficiency. The maintenance of a suitable pH can usually
be effected by placing in the bath a suitable buffer, i.e., one which,
as far as the catholyte is concerned, will react with the liberated
hydroxyl ions, and in so doing, will produce very little change in

hydrogen-ion concentration. R. Thompson (*Trans. Amer. Elec-trochem. Soc.*, 1922, **41**, 344) has investigated the effects of adding boric acid, sodium fluoride, and free hydrofluoric acid to nickel-plating baths. His results are given in Fig. 160, which shows the effect on the *p*H of adding either 0·2 N-H_2SO_4 or 0·2 N-NaOH to 50 c.c. N-$NiSO_4$ containing the " buffers " marked on the diagram. Maximum efficiency was obtained at about *p*H 6, which is just below that at which the precipitation of nickel hydroxide
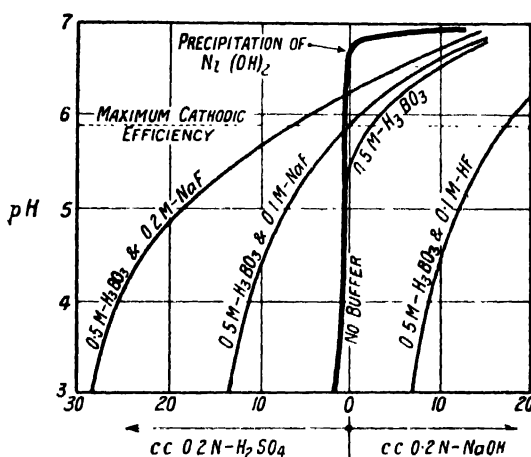
Fig. 160.—The Effect of Buffers on *p*H of Nickel Plating Solutions (N-$NiSO_4$).

begins. The curves show that by using boric acid appreciable amounts of alkali or acid may be added before the acidity is increased by one *p*H unit. It is often the practice to put ammonium chloride in a nickel-plating bath, about 0·25 N, in addition to the boric acid.

Fig. 161 gives the results of Thompson (*loc. cit.*) and Montillon and Cassel (*Trans. Amer. Electrochem. Soc.*, 1924, **45**, 266) on the importance of the *p*H of nickel and cobalt plating baths in promoting the greatest efficiency. Curves A, B, C, and D refer to nickel (Thompson), and E and F to cobalt (Montillon and Cassel). For A and B, the bath was N-$NiSO_4$, 0·25 M.-H_3BO_3 and 0·1 N-NaCl, the current density for A being 1·5 amp./dm² and 0·2 amp./dm² for B. C and D refer to baths containing 0·1 N-NaF in place of the sodium chloride, current densities being 1·5 and 0·2 amp./dm² respectively. E and F refer to baths containing 312 grams of cobalt sulphate per litre, 14 grams of sodium fluoride, and boric acid nearly to saturation, the current

densities being 3·0 amps. for E, and 5 amps. for F, per square dm. In every case, maximum efficiency, nearly 100 per cent., was obtained when the baths were at pH 6, nickel hydroxide precipitating at pH 6·7 and cobalt hydroxide at pH 6·8. Montillon and Cassel found that nickel plating carried out at pH 6 resulted in a very dense, greyish-white, adherent smooth surface having no gas streaks or pits. At pH 4·5 the plating was fairly good, though it had a few gas streaks, but at pH 3·5 there were many gas streaks,
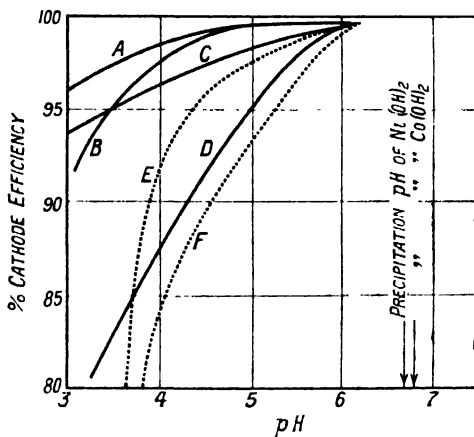
Fig. 161.—Relationship between Cathode Efficiency and pH of Nickel and Cobalt Plating Solutions.

and the deposit tended to peel off. In the cobalt work, the plating was excellent at pH 6, but became unsatisfactory below pH 4·5. Thompson states that nickel deposits show evidence of blistering, cracking, and curling when obtained from a bath at pH 6·3 to 6·5.

Foerster and Krüger (*Z. Elektrochem.*, 1927, **33**, 406) have investigated the electrolysis of nickel sulphate solutions containing varying amounts of nickel chloride and 2 per cent. of boric acid between nickel electrodes at 20° C. As the efficiency of the electrolysis as a whole depends upon the efficiencies of the two poles, the rate of dissolution of the anode should be equal to that of the nickel deposition on the cathode. It is essential to prevent the anode from acquiring a passive state by including in the bath sufficient nickel chloride. The chloride ions interact with the oxide film covering the anode and produces a condition of " temporary passivity." By employing a low current density, or keeping the chloride concentration high, they found that the anode could be kept active continuously and it dissolved with high

current efficiency between potentials + 0·40 and + 0·58, the potential of the normal hydrogen electrode being taken as zero. The *p*H of the electrolyte gradually increased. Good cathodic deposits were obtained at *p*H values below 5·5, which are somewhat lower than those found by previous workers. Foerster and Krüger also found that high *p*H values lead to flaking and cracking through the development of hydroxide precipitate within the metal, which also enables bubbles of hydrogen to adhere and so cause pitting. (*Cf.* O'Sullivan, *Trans. Faraday Soc.*, 1930, **26**, 89, 533, 540.) According to Phillips (*Trans. Amer. Electrochem. Soc.*, 1930) nickel deposits of thicknesses greater than 0·0125 mm. tend to become burned, to crack, or to peel if formed at *p*H 6. Lowering the *p*H causes superior metal to be deposited, the greatest gain being obtained at *p*H 2 or lower, even though the cathode efficiency is reduced to 70-75 per cent.

For high-speed bright nickel-plating Pinner and Kinnaman (*Month. Rev. Amer. Electroplaters' Soc.*, 1945, **32**, 227) prefer sulphate baths that contain appreciable amounts of nickel chloride. The optimum conditions are : *p*H 1·5, 46° C. and C.D. = 100 amp. per sq. foot.

In comparing low *p*H baths with those of high *p*H, Halls (*Metal Treat.*, 1944–45, **11**, 235) states that the former are freer from sludge, are cleaner to operate and permit the use of higher C.D., but the anode efficiency may exceed that of the cathode, and generally their flexibility is less than those of high *p*H. One disadvantage of the low *p*H nickel-plating bath is its lower " throwing-power," but this can be enhanced somewhat by raising the C.D. and the temperature. (Harr., *Trans. Electrochem. Soc.*, 1933, **64**, 203 ; Flowers and Warner, *ibid.*, 1932, **62**, 322.)

, Macnaughton and Hothersall (*Trans. Faraday Soc.*, 1935, **31**, 1168) find that the electrodeposits of nickel and of cobalt from high *p*H baths are harder (Brinell Hardness) than those from low *p*H baths. The finer grain-size they attribute to inclusions of basic salts in the metal which interfere with crystal growth. Alkali metal ions in the bath tend to coagulate basic salt suspensions and so favour the formation of these basic inclusions, which thereby assist in producing harder metal plate. Chloride ions have the reverse effect. Nickel baths of *p*H > 5 give harder deposits at greater cathode efficiency. Pitting is also less. (Macnaughton, Gardam and Hammond, *ibid.*, 1933, **29**, 729.) Annealing in vacuo at 1000° C. reduces the tensile strength of the deposits formed above *p*H 5 to an extent greater than that of deposits formed below *p*H 5. (Gardam and Macnaughton, *ibid.*, 755.)

The advantages of employing a depolariser, chromic acid, in nickel-plating baths have been studied by Hothersall and Hammond (*ibid.*, 1935, **31**, 1574), who observed that, whilst small amounts of chromic acid cause a marked reduction in cathode efficiency, the deposits are more lustrous, especially at high pH values. Larger quantities decrease the cathode efficiency considerably and also give exfoliated, burnt deposits, or may even prevent deposition entirely.

Ballay (*Compt. rend.*, 1934, **198**, 1494 ; **199**, 60) has investigated the deposition of nickel from chloride baths at pH values ranging from 3·6 to 9·8. The high pH baths were made possible by using alkali citrate to prevent the precipitation of nickel hydroxide. The deposits from alkaline baths were fragile. Cathode efficiency was higher, *e.g.*, at pH 5·0, 59·2 per cent. ; at pH 9·6, 94·2 per cent.

Nickel chloride baths are preferred by Fedoteev and Kinkuski (*Z. anorg. Chem.*, 1935, **224**, 337), who recommend a bath containing not less than 40 grams Ni per litre at pH 6·2–6·8, the temperature being 70°–80° C. and the C.D., 5 amp./dm².

Impure cobalt is of 98·4–98·7 per cent. purity. It can be refined electrolytically to a purity of 99·76 per cent. and according to Oldach (*Met. and Alloys*, 1943, **17**, 967) this can be done by electrolysing a solution of cobalt sulphate, sodium chloride and boric acid, adjusted to pH 4·5–5·0, at a temperature of 55° C. and a C.D. of 4·5 amp. per sq. dm. The crude cobalt, which serves as anodes, should be in the form of short cylinders, 0·5 inch in diameter. The cathodes consist of rotating stainless steel cylinders.

Alloys of phosphorus and either cobalt or nickel, which increase in hardness on heating and are more resistant to chemical attack than the respective metals, may be deposited from cobalt or nickel chloride baths, to which either phosphoric or phosphorous acid has been added, and their pH adjusted to 0·5–2·0. The alloys are metallic in character though they may contain as much as 15 per cent. of phosphorus (Brenner, Couch and Williams, *Plating*, 1950, **37**, 36, 161).

Zinc has been deposited from a zinc sulphate solution containing partly neutralised acetic acid as the buffering agent, but Thompson (*Trans. Amer. Electrochem. Soc.*, 1926, **50**, 219) has called attention to the fact that acid zinc plating baths have low " throwing power " and that higher current densities could be employed if the plating were carried out from zinc chloride or sulphate solutions of about 2 N, and being 3 to 4 N with respect to either sodium or ammonium chloride and 0·25 N

with respect to either aluminium chloride or sulphate. He was able to use 5 amps./dm² with stationary cathodes and up to 15 amp./dm² with moving cathodes. Partly neutralised acetic acid could also be used in place of the aluminium salt. The most satisfactory reaction of a zinc sulphate bath containing sodium acetate and a very small amount of gum arabic has been found by Cocks (*Metal Ind.* (London), 1930, **36**, 385, 388), to be *p*H 4. Table 180 shows that zinc hydroxide precipitates at *p*H 7·0, whereas aluminium hydroxide does so at *p*H 4·2 from sulphate solutions, though from chloride solutions actual precipitation is usually delayed until higher *p*H's are obtained. Thompson found boric acid to be useless, as would be expected from its great weakness, and he adds that though the aluminium salt in behaving as a buffer might cause aluminium hydroxide to separate, the presence of the hydroxide had no deleterious effect on the plating. The appearance of a precipitate, moreover, gave a clue of the *p*H of the bath and it also tended to protect the anode from attack. Aluminium salts appear to have been used in zinc plating baths first in 1854. The cathode efficiency may by their use become nearly 100 per cent.

Cadmium plating is generally carried out from cyanide baths, which contain free sodium cyanide (*i.e.*, in excess of the amount required to form the complex cyanide, $Na_2Cd(CN)_4$), and alkali. Too low a *p*H leads to blistered deposits (Springer, *Z. Elektrochem.*, 1936, **42**, 732). Incidentally, similar conditions apply to complex cuprous cyanide baths, the complex salt being $K_2Cu(CN)_3$. The *p*H should not fall below 10·7, and for uniform, fine crystalline deposits the *p*H should be higher than 12·5. (See also Thompson, *J. Res. Nat. Bur. Stand.*, 1940, **24**, 423 ; Research Paper, R.P. 1291).

Cadmium sulphate is now finding application as an electro-depositing bath. According to Wernick (*Trans. Electrochem. Soc.*, 1932, **62**, 75), it is buffered at *p*H 5·6 with boric acid, sodium chloride also being added. Increasing the C.D. up to 4·5 amp./dm² decreases grain-size and improves adhesion and the ease with which the metal can be burnished. It also affects the cathode efficiency. The deposits are different from those obtained from cyanide solutions. The range, *p*H 5·5–6·6, gives satisfactory coverings (*Trans. Faraday Soc.*, 1935, **31**, 1240).

The electro-deposition of iron has not yet gained very great technical importance, though it was used during the war of 1914–18 for restoring worn aircraft parts. W. E. Hughes (*Trans. Amer. Electrochem. Soc.*, 1921, **40**, 185) gives a complete summary

of the baths which have been employed, some of which contain ammonium salts as buffers, whereas in others, particularly in ferrous chloride solutions, a little acid is included. It appears that the ferrous sulphate baths should contain only a very small amount of free acid, for too much acid reduces the cathode efficiency in a marked manner, whereas chloride baths should be neutral. The ratio $[Fe^{··}]/[H^·]$ must be large and the deposition carried out at an elevated temperature. Adjustment to pH 2·5 of ferrous sulphate and chloride baths by adding sulphuric acid has been found by Pike and co-workers (*Amer. Inst. Min. Met. Eng. Tech. Pub.*, 1930, No. 268) to be of advantage.

The electro-deposition of manganese has received some attention, particularly by Grube and Metzer (*Z. Electrochem.*, 1923, **29**, 17, 100) and Allmand and Campbell (*Trans. Faraday Soc.*, 1924, **19**, 559; 1925, **20**, 379). Bunsen obtained electrolytic manganese from manganous chloride solution as early as 1854. Grube and Metzer, using baths of 6–7 N-MnCl$_2$, 1·5 N-NH$_4$Cl and 0·1 N-HCl with a current density of 20 amp./dm^2, obtained a current efficiency of 50–60 per cent. Allmand and Campbell obtained lower efficiencies, but they secured their best results when the pH lay between 6 and 8. When 0·36 per cent. or more H$_2$SO$_4$ was present in the catholyte the manganese deposition ceased. A perusal of Fig. 159 will make the fact that manganese can be deposited electrolytically appear surprising, but it must be stated that the baseness of manganese is somewhat compensated for by its high hydrogen over-voltage.

Some attempts have been made to regulate the hydrogen-ion concentration of chromic acid baths used in chromium plating, but owing to the nature of the electrolyte it is unlikely that any great success will be obtained. The process, first studied by Bunsen, of depositing chromium from tervalent chromium salt solutions has been the subject of two patents. In the process protected by the Langbein-Pfanhauser-Werke A.-G. (B.P. 301,478) the pH is maintained between 4 and 6 by the inclusion of sodium salts of either tartaric, citric, oxalic or phenol-sulphonic acids. On referring to Chapter XXIV, it will be seen that chromium hydroxide begins to precipitate at pH 5·3 under normal conditions, but the use of hydroxy-acids renders it possible to exceed this pH value without the occurrence of precipitation. Britton and Westcott (*Trans. Faraday Soc.*, 1932, **28**, 627) have found that by adding alkali in amounts insufficient to cause the precipitation of the chromium hydroxide and thereby raising the pH, better deposits and greater efficiencies can be obtained than by using a simple tervalent chromium salt.

Effect of Gelatin on Electro-deposition.

" Addition agents," usually of an organic colloidal nature, are sometimes employed in electrolysis baths for the purpose of improving the physical character of the deposited metal and sometimes to facilitate deposition. Thus Mathers and McKinney (*Trans. Amer. Electrochem. Soc.*, 1915, **27**, 131) recommend the addition of Barbadoes aloes to electrolytes containing lead nitrate and acetic acid in order to obtain satisfactory even deposits, and in the Betts Process for the Electrolytic Refining of Lead (*Trans. Amer. Electrochem. Soc.*, 1905, **8**, 64) in which the bath is composed of a solution of lead in hydrofluosilicic acid, gelatin in the form of glue is included. This causes a slight increase in the polarisation of the cathode and thus increases the cathode efficiency and the formation of a smooth deposit. Gelatin has also been observed to raise the cathode potential when copper is being deposited from acid solutions (Le Blanc, *Elektromotorische Krafte der Polarisation, Halle,* 1910 ; E. Müller and Bahntje, *Z. Elektrochemie,* 1906, **12**, 317 ; Siewerts and Wippelmann, *Z. anorg. Chem.*, 1915, **91**, 1). This increase in polarisation is also reflected in the change in the texture of metallic deposits obtained, especially in the production of more dense and smooth, fine-grained metal. Pring and Tainton (*J. Chem. Soc.*, 1914, **105**, 710) found that the efficiency was enhanced by the addition of gelatin in the deposition of zinc from a strongly acid electrolyte using a very high current density of 20-100 amperes per square decimetre. W. E. Hughes (*Metal Ind.* (London), 1924, **25**, 269), however, found that in the electrolysis of zinc sulphate solutions gelatin had practically no effect upon the structure of the deposit, but that it had a marked effect when the solution was acidified with sulphuric acid. The former solutions were alkaline to Congo red, *i.e., p*H > 4, and the latter acid, *i.e., p*H < 4. It appears, therefore, that under certain conditions of acidity the use of gelatin or glues gives rise to improved deposits, though it should be mentioned that Mathers (*Trans. Amer. Electrochem. Soc.*, 1924, **46**, 84) claims to have found no improvement in the tin deposited from tin silicofluoride bath containing glue.

Frölich (*Trans. Amer. Electrochem. Soc.*, 1924, **46**, 67) has directed attention to the fact that in general it is only when the gelatin is added to an electrolyte of high hydrogen-ion concentration that the gelatin is found to have a beneficial effect. This, he argues, is in harmony with the amphoteric nature of gelatin, its isoelectric point being at *p*H 4·7. Thus in acid solutions gelatin combines with the acid, forming salts, and therefore,

when the solution is subjected to electrolysis, the gelatin migrates towards the cathode where it accumulates and offers additional resistance to the transportation of the inorganic cations up to the cathode surface. This increases the cathodic polarisation. It is highly probable that in ordinary electro-depositions the pH of the film of solution directly in contact with the surface of the electrode is different from that of the main body of the solution. Thompson (*Trans. Amer. Electrochem. Soc.*, 1922, **41**, 333) states that this is the case in the deposition of nickel from an acid electrolyte, and Eiffe (*Thesis, Massachusetts Institute of Technology*, 1924) cited by Frölich, has observed in zinc deposition experiments that for a certain zinc salt concentration a pH close to 6·2 existed next to the cathode whereas the acidity of the main body of the electrolyte varied from pH 6·2 to pH 2·5. That a gelatin film is formed on the cathode may, as Frölich states, be inferred from the increase in the size of the gas bubbles which emerge from the cathode and the difficulty with which they break loose and escape. Moreover, in acid electrolytes gelatin has no effect on the anode. As the pH of gelatin decreases from 4·7, the swelling in water increases until pH 3·2 is attained after which the swelling becomes less again. Hence the density of the cathodic film of gelatin, and consequently the impeding effect which it will have on the maintenance, by diffusion and convection, at a high concentration of electrolyte immediately around the cathode, will depend upon the local pH. Blum and Rawdon (*Trans. Amer. Electrochem. Soc.*, 1923, **44**, 397) state that coarse crystalline deposits of metals are produced by having an excess of metal ions in the catholyte, whereas low metal-ion concentrations with a large reserve of undissociated salt, *e.g.*, complex cyanides, are conducive to the formation of smooth, fine-grained deposits. Frölich suggests that the latter conditions exist when the cathode is closely surrounded by a film of gel of high viscosity, for its presence restricts considerably the passage of the electrolyte to the cathode surface except by those cations which are in the act of being deposited. If too much gelatin be used and the pH of the cathode film be such as to make the gelatin deposited therein dense, it is conceivable that circumstances may arise when the resistance encountered by the cations on the point of being deposited will become so great as to force the metal to deposit within the gelatin film itself. Some little co-precipitation of gelatin with the copper takes place from acid copper baths and in practice it is necessary to add fresh quantities of gelatin from time to time. Frölich is of the opinion that while the introduction of gelatin into the deposit certainly affects its appearance, co-precipitation is not essential in order

to improve the texture of the deposited metal. The low acidities of the cathode liquid films in the case of zinc and nickel, usually of *p*H greater than 4·7, prevent the formation of gelatin layers on the cathode, the gelatin migrating to the anode, and so the gelatin is without any appreciable effect on the deposited metal. When acid solutions are used the gelatin may become entangled in the deposit. The deposits from solutions of low acidity have in some cases been found to contain organic matter, probably as the result of the catalytic decomposition of the gelatin at the surface of the electrode.

Schlötter (U.S.P., 1,972,693) claims that brighter and better nickel plate may be obtained by using colloids of lower molecular weight—less than 5,000. Thus nickel benzene disulphonate or nickel naphthalene sulphonate when added to nickel sulphate or chloride baths, buffered at *p*H 2·5–4·5, yields bright deposits, the average grain-diameter being less than 0·0001 mm. Polishing is unnecessary, even when the nickel layer is to form the basis for chromium.

Anodic Coatings.

Smooth, adherent deposits, which vary from a dirty green to a shiny black, can be formed on magnesium alloys anodically by electrolysing in a bath buffered at *p*H 4·0–4·8 by NaH_2PO_4 and $NaHCrO_4$. The deeper coloured coatings are formed on the alloys having the larger aluminium contents (Buzzard and Wilson, *J. Res. Nat. Bur. Stand.*, 1937, **18**, 83).

CHAPTER XXXIII

THE IMPORTANCE OF HYDROGEN-ION CONCENTRATION IN THE PRELIMINARY STAGES OF LEATHER MANUFACTURE

In this chapter an attempt is made to show how the efficiency of many reactions, to which the proteins present in skins have to be subjected before the skins are ready for tanning, depends upon the hydrogen-ion concentration in the various liquors, such as those employed for " soaking," " liming," " bating " and " deliming," " pickling " and " drenching." The developments in biochemical research have shown that in order to secure (or to avoid) the optimum activity of the enzymes and bacteria involved in leather manufacture specific ranges of hydrogen-ion concentration have to be established.

Epitome of Stages of Leather Manufacture.

It will be an advantage to give at the outset a short *résumé* of the stages through which a skin has to pass in order that it may become an imputrescible, pliable, and durable leather. Before the skins are actually tanned, they have to undergo several treatments, so that the fibres are in the best condition to receive the tannage and all possibilities of putrefaction are eliminated. These treatments comprise the " preservation," and, when necessary, the " disinfection " of the skin, " soaking and fleshing," in which all adipose tissue and adhering flesh are removed, and the skins receive a general trimming which involves the removal of ears, cheeks, hoofs, and tails. One of the objects of soaking, besides to facilitate " fleshing," is to render the skins free from soluble globulins and proteins. The next stage is that of " unhairing and scudding," in which the hair is first loosened from the skin, which may be effected by a variety of methods. Then the hair is mechanically removed or scraped off with a blunt and somewhat curved two-handled knife on a sloping rounded " beam " of wood or metal. The commonest method of removing the hair and the epidermal layer now used is that known as " liming " in a saturated solution of slaked lime, until the hair and epidermis have become so loose that they may be rubbed off with very little difficulty. The alkaline solution also has the effect of causing the skin to

swell or " to undergo plumping," due to the imbibition of water.
The skin, however, is not yet in a condition suitable for tanning,
for the bundles of fibres in the skin, although more or less separ-
ated through the swelling of the skin, are held together by elastic
protein fibres, the chief protein being " elastin."   Again, the skin
is somewhat impervious to liquors in its now rubbery or plump
state, and consequently before the adsorption of tanning liquors
becomes possible the skin must be subjected to yet another
important treatment to remove the undesirable proteins, such as
" elastin," and at the same time to diminish its bulk or swelling ;
in technical terms to bring about " falling."   This process is that
of " bating," and originally consisted in keeping the unhaired
skins in a warm infusion of hen or pigeon dung, or in the case of
light skins, of dog dung when it was called " puering," until they
had become extremely relaxed and flaccid, or fallen, and became
so soft as to retain the impression of the thumb and finger, and
sufficiently porous that air could be forced through them.

This objectionable and filthy process is gradually being super-
seded by the use of the tryptic enzymes present in pancreatin,
obtained from the pancreas of animals, in conjunction with
ammonium chloride as the deliming agent.   Thus Boidin and
Effront (U.S.P., 1,812,921) carry out bating and unhairing with
an enzyme preparation, first at *p*H 8–9 and subsequently in
slightly acid solution.   A similar process, *viz.*, the " Azazym,"
is used for unhairing goat skins which are first swollen in approx.
o·1 N-NaOH and then treated with o·1 N-NaHCO₃.   When *p*H
8·9 is reached, *trypsin* is added and the skins are left overnight.
Whilst the process does not cause the protein which fastens the
hair and epidermis to the corium to dissolve completely, it dis-
integrates the proteins into fragments and so reduces the time
required for bating (Turley and Morse, *J. Amer. Leather Chem.
Assoc.*, 1932, **27**, 282).   In the older process the deliming agent
was the mixture of weak organic acids liberated by the decom-
position of elastin by the enzyme action.   Before finally subjecting
the skin to the tanning liquors, it is usually either " drenched "
or " pickled," the former being preferable if vegetable tanning
liquors are to be subsequently used, and the latter if chrome
liquors ;   in fact, pickling prior to chrome tanning is almost
imperative.

" Drenching," which may sometimes take the place of bating,
is carried out by placing the skin in a liquor containing 5 to 10
grams of bran per litre at 30° to 35° C., and allowing fermentation
to ensue.   Gases, such as carbon dioxide, hydrogen and nitrogen
are evolved, and also organic acids—*e.g.*, formic, acetic, butyric,

and lactic acids, are produced which render the skins acidic in reaction. Under certain conditions this may be very beneficial, but as the treatment is of a somewhat uncertain character, careful control is necessary, and also care must be taken to ensure that the skins do not get damaged by the formation of gases inside the skin, which, in forcing their way through the grain surface, make perforations. Too high a temperature, especially if accompanied by the formation of too much acid, may also cause some of the chief protein, collagen, in the skin to decompose and give an unsatisfactory spongy leather. Organic acids and sometimes hydrochloric acid are often used in place of bran liquors.

" Pickling " is often resorted to when the skins are not to be tanned immediately, and also when they are to be chrome-tanned. It used to be the practice to treat the skins, limed or bated, with a dilute solution of sulphuric acid until the desired amount of swelling had been obtained, and then to repress the swelling somewhat by immersion in a saturated brine solution. Nowadays, pickling can easily be controlled chemically, merely by titration to methyl orange, and one pickling solution, therefore, is used which often contains very dilute sulphuric acid and sodium chloride to the extent of about 1 g.-mol. per litre. The object of both " drenching " and " pickling " appears to be to bring the acidity of the skins to the reaction most convenient for efficient tanning, and as will be shown later, the proper adjustment of acidity is a question of considerable importance in tanning.

It is now being realised that on these preparatory processes the ultimate success of the tanned leather depends. Pleass (*J. Soc. Leather Trades Chemists*, 1935, 19, 4) points out that the best microscopic appearance of the leather is to be obtained from a pelt that has been pickled in acetic acid. To ensure efficient pickling, the pH of the aqueous extract should lie between 2·0 and 2·4.

The process of tanning was formerly carried out entirely by means of aqueous extracts of tanning derivatives obtained from various barks. Oak bark extracts are preferred on account of the firmness and solid nature of the resulting leather, though hemlock bark finds great favour in America for the manufacture of heavy leather. For sole leather the tannins of chestnut and oak woods are often used in conjunction with other substances. Care must also be exercised to use only those tannin extracts from which the tannin will not be precipitated when the skins are placed in them, such as would happen if an unsatisfactorily delimed skin were immersed in a quebracho extract. Another important, and, indeed, a very valuable means of tanning light skins in particular,

is by means of basic chrome liquors, a process which will be discussed fully in Chapter XXXIV. After tanning, the leathers are subjected to various finishing operations, such as neutralising, fat-liquoring, dyeing, and in the case of chrome-tanned leather some type of filling will be necessary to compensate for the so-called " emptiness."

Collagen and Gelatin.

Having outlined the various stages of leather manufacture, we shall now devote our attention to the physical chemistry of the subject, so that, when reviewing the several treatments in greater detail, we shall be able to get a better insight into the reasons for the various procedures and, moreover, to see why a rigid regulation of the hydrogen-ion concentration of the solutions furnishes an excellent method of controlling the whole process of manufacture.

Skin comprises several proteins. Collagen is the most important constituent of the derma, being the protein in the white fibres of the connective tissue. It is these fibres which determine the quality of leather which can be produced. The keratins are found in the epidermis, and the hair or wool ; the mucins, albumins, and globulins in small amounts in the derma ; and elastin in the yellow elastic fibres. Other proteins are also present in the derma, but they have not hitherto received names. All these types of proteins, with the exception of collagen and some of the unidentified proteins, are eliminated in the processes prior to tanning ; thus the albumins disappear on treatment with water, they alone being soluble, the globulins are soluble in dilute sodium chloride solutions, the mucins in dilute alkaline solution, the keratins though soluble only in strongly alkaline solution are largely removed mechanically, after the appropriate putrefactive fermentation has been allowed to take place, and the elastin by digestion with trypsin. According to Thomas and F. L. Seymour-Jones (*J. Amer. Chem. Soc.*, 1923, **45**, 515) collagen is also attacked by trypsin when the action is allowed to take place at 40° C. at *p*H 5·9, but the amount of collagen which becomes soluble in the bating or modified bating processes is generally very small. Collagen, in the form of Hide Powder, can be prepared from skin in the laboratory by a method parallel to that used in preparing the skin for tanning. The skin is prepared by cutting extraneous tissue away, after which it is thoroughly washed and the soluble proteins extracted with several changes of 10 per cent. sodium chloride solution in a shaking machine. The hair and epidermis is now loosened by immersion in a saturated solution of slaked lime containing about 0·1 per cent. sodium sulphide for several days

with frequent agitation, and when sufficiently loose the hair and outer skin is scraped away with a knife. This exposes the grain surface which is then removed. After the lime has been extracted by washing, the elastin fibres may be dissolved out by digestion at 40° C. with pancreatin solution containing 1 gm. per litre and suitably buffered to the pH value of bating liquor, *viz.*, *ca.* pH7. Wilson (" The Chemistry of Leather Manufacture," 1923, p. 72) gives 2·8 gm. NaH_2PO_4 and 18 c.c. N-NaOH per litre, which on calculation is found to give a pH of 7·4. After cutting up into small pieces the skin is soaked in water and treated with hydrochloric acid until faintly acid to methyl orange and washed first in running water, then with alcohol and finally with xylene, after which it is air-dried and crushed to a fibrous powder.

Upon prolonged heating at about 70° C. with water, collagen passes into gelatin, though the nature of the change which takes place is still a question of doubt. Hofmeister (*Zeitsch. physiol. Chem.*, 1878, **2**, 299) held that it was one of dehydration and that gelatin was the anhydride of collagen, whereas Emmett and Gies (*J. Biol. Chem.*, 1907, **3**, 33) suggested it was a case of intramolecular rearrangement. As pointed out by later workers there is good evidence in support of both contentions. Much of the waste skin of the tannery is converted into gelatin or into the more crude form of glue. Bogue (*Ind. Eng. Chem.*, 1923, **15**, 1154) has studied the conversion of collagen into gelatin with respect to ranges of pH which should be maintained during boiling. He found that the pH should be kept either between 3 and 4 or 7·5 and 8·5. Between pH 4·5–6·0 the conversion proceeds too slowly, while at values below 3 or above 8·5 the gelatin, which is formed, rapidly breaks down. It is best to use about 12 parts of water to each part of dry collagen and to keep the temperature at 80° C. for about 8 hours. The previous swelling of the stock may best be carried out with lime or lactic acid, but excess of reagent must be removed before heating. Bogue favours the view that collagen is not a simple anhydride of gelatin but rather a product of chemical condensation. Hudson and Sheppard (*Ind. Eng. Chem.*, 1929, **21**, 263) suggest the following specifications for so-called standard gelatin. It should be prepared from well-limed calf-skin and only the first aqueous extract should be used which should be made at about 54° C. Its isoelectric point should be pH 4·7–4·9 and the ash-content should be less than 0·05 per cent. Among the other points are viscosity, jelly-strength, light absorption.

The analytical data given in Table 201 show that collagen, as derived from various animal skins, is of a fairly constant composi-

TABLE 201

COMPOSITION OF COLLAGEN

Skin.	Per Cent. C.	Per Cent. H.	Per Cent. N.	Per Cent. O.
Ox (average)	50 5	6 5	17·8	25·2
Calf	50·2	6·5	17·8	25·5
Camel	50·0	6·4	17·7	25·9
Horse	50·2	6·4	17·9	25·5
Pig	49·9	6·3	17·8	26·0
Rhinoceros (average)	50·2	6·4	18·0	25·4
Goat	50·3	6·4	17·5	24·8
Deer	50·3	6·4	17·4	25·9
Sheep	50 2	6·5	17·1	26·2
Chamois	50·1	6·4	17·3	26·2
Dog	50·3	6 5	17·0	26·2
Cat	51·1	6·5	17·1	25·3

tion. The figures were taken from a paper by von Schroeder and Pässler (*Dingl. polytech. J.*, 1893, **11–13**, 287) and refer to water-free products.

The composition of collagen bears a striking similarity to that of gelatin. Table 202 gives typical analyses of gelatin. It does not, however, give the sulphur content, which is always very small. Of the analyses recorded since 1843, the mean nitrogen content of gelatin is found to be 18 per cent.

TABLE 202

COMPOSITION OF GELATIN

Per Cent. C.	Per Cent. H.	Per Cent. N.	Per Cent. O.	Chemist.
49·9	6·4	17 7	26·0	Rakusin, 1922.
50·0	6·5	17·5	26·0	Fremy, 1854.
50·0	6·7	18·3	25·0	Schutzenberger, 1876.

Attention has specially been directed to the relationship which subsists between collagen and gelatin, for the latter substance, being easier to experiment upon, has received much more attention. Its importance from the point of view of leather chemistry is great, inasmuch as it has many properties and reactions in common with collagen. This is true with regard to their behaviour towards tanning agents, and towards both acids and alkalis. The application of the results of physico-chemical researches on gelatin to the chemistry of leather has thrown much light on many of the

processes, and for this reason we shall now pay some attention to them. Hardy showed in 1899 that proteins are soluble in acids and then become positively charged, whereas in alkalis they dissolve but become negatively charged. At some intermediate stage when they carry no electric charge, a point is reached which he called the "isoelectric point," when they also possess minimum solubility. The location of the isoelectric point, though formerly a matter of academic interest, has now become a subject of technical importance, and with the development and application of potentiometric methods, it has become an easy matter to ascertain the pH corresponding to the isoelectric point. From a qualitative point of view, proteins may be considered as complex amino-acids, thus $R\underset{\diagdown NH_2}{\overset{\diagup COOH}{}}$, and therefore react with acids in solutions more acid than that of the isoelectric point, as bases, e.g., $HOOC.R.NH_2 + HCl \rightarrow HOOC.R.NH_2.HCl$; and with bases in solution more alkaline than that of the isoelectric point, e.g.,

$$NH_2.R.COOH + NaOH \rightarrow NH_2.R.COONa + H_2O.$$
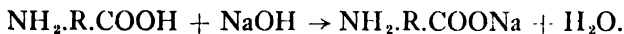
Proteins may also be regarded in a general way as Zwitterions, $\overset{+}{NH_3}R\overset{-}{COO}$ (see, e.g., Page, *J.A.L.C.A.*, 1933, **28**, 100 ; Page and Holland, *ibid.*, 1937, **32**, 78, who have interpreted the action of tannins on collagen in terms of Zwitterions).

Gelatin, however, does not react with a definite amount of either acid or alkali. The amounts depend upon the pH of the solution and the previous treatment of the gelatin (*cf.* Lloyd and Mayes, *Proc. Roy. Soc.*, B., 1922, **93**, 69 ; Hitchcock, *J. Gen. Physiol.*, 1921–2, **4**, 733 ; Atkin and Douglas, *J.I. Soc. Leather Trades Chemists*, 1924, **8**, 584). The author has carried out some potentiometric titrations on gelatin solutions which had undergone certain previous treatments. Besides giving some idea of the extent to which gelatin is able to combine with acids and bases, they throw some light on the change which gelatin undergoes when subjected by protracted heating with water. After such treatment the gelatin loses its power of gelatinisation and therefore becomes useless for adhesive purposes.

Hydrogen Electrode Titrations of Gelatin.

In recent years it has been realised that gelatin prepared by heating either collagen or ossein with water contains some decomposition products and therefore requires purification. Thus

Sheppard, Sweet, and Benedict (*J. Amer. Chem. Soc.*, 1922, **44,** 1858) purified gelatin by electrolysing the jelly and precipitating the gelatin from it with acetone. The gelatin used by the author was purified by the method described by Knaggs and Schryver (*Biochem. J.*, 1924, **18**, 1079), which is one of electrodialysis of a gelatin solution through a collodion membrane until the gelatin becomes flocculated when it is redissolved and reflocculated until the nitrogen content of the supernatant liquid becomes extremely small. In this way a gelatin was obtained free from electrolytes and also from soluble nitrogenous contaminants.

Solutions (1 gram in 100 c.c. water) of this product had a *p*H lying between 4·7–4·8. In one case 100 c.c. were titrated electrometrically using the hydrogen electrode with 30 c.c. N/10-HCl, and then back-titrated with N/10-NaOH at 20° C. The back-titration curve obtained is shown in Fig. 162, marked " purified." Another 100 c.c. of 1 per cent. purified gelatin solution were boiled under a reflux condenser for 24 hours, cooled to 20°, 30 c.c. N/10-HCl added, and similarly titrated. The curve obtained is labelled " boiled." Another NaOH titration was carried out on a 1 per cent. solution of Coignet's " Gold Label " gelatin, containing the same amount of HCl, and the curve obtained is labelled " ordinary." Fig 162 also contains for the purpose of comparison, the titration curve of 130 c.c. of a hydrochloric acid solution, containing 30 c.c. N/10-HCl, with N/10-NaOH. The position of the gelatin curves corresponding to its reaction as a base in forming gelatin hydrochloride show that as far as the basic groups in gelatin are concerned there appears to be very little difference, if any, between the gelatins in the three solutions. The figures placed between the HCl and gelatin curves give the number of cubic centimetres of N/10-HCl which reacted with 1 gram of gelatin at the various *p*H's, and are simply the differences between the amount of hydrochloric acid actually added to the gelatin to give any particular *p*H and the amount of hydrochloric acid required alone to give the same *p*H, the unhydrolysed gelatin hydrochloride being taken as neutral. Thus it is seen that in the dilution used at *p*H 2, 1 gram of gelatin combined with 8·4 c.c. N/10-HCl ; at *p*H 2·5, 8·1 c.c. ; at *p*H 3, 7·4 c.c. ; and thereafter the amount rapidly fell off to *p*H 4·7, the isoelectric point, when it became zero. Similar observations have been made by Loeb (*J. Gen. Physiol.*, 1920–1, **3**, 100), Hitchcock, Lloyd and Mayes (*loc. cit.*), Lloyd and Bidder (*Trans. Faraday Soc.*, 1935, **31**, 865), Atkins and Douglas. Atkin and Campos (*J.I.S.L.T.C.*, 1924, **8**, 408 ; *J.A.L.C.A.*, 1924, **19**, 498) titrated hide powder by means of indicators and showed that it too, below the isoelectric

point, combines with acids in amounts depending upon the pH finally set up.

The remaining parts of the curves given in Fig. 162 indicate the nature of the reactions of gelatin as an acid.   The figures give the number of cubic centimetres of N/10-NaOH, which united with 1 gram of gelatin in forming sodium gelatinate.   At pH 8, 3·7 c.c. of alkali had combined and at pH 10, 5·3 c.c.   Greater amounts of alkali were required in the case of gelatin, which had undergone
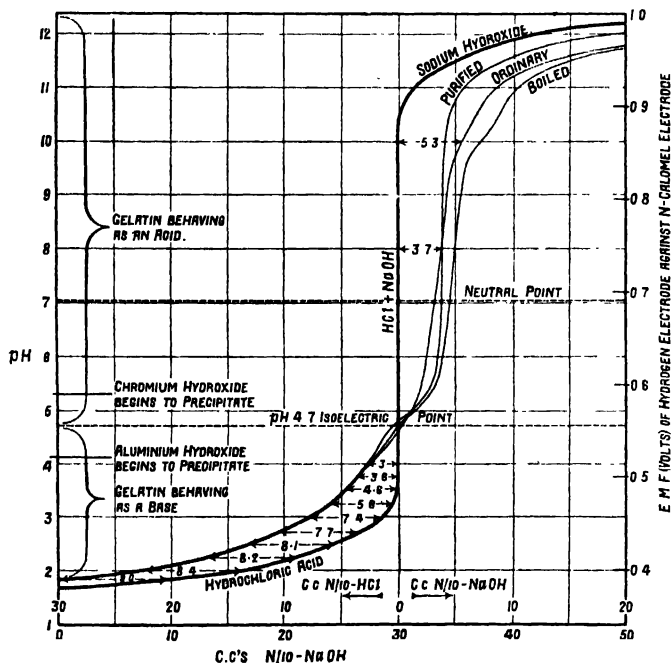
Fig. 162.—Hydrogen Electrode Titration Curves of Gelatin.

protracted boiling.   It will be observed that the curve, corresponding to purified gelatin, shows no inflexion between pH 10-11, whereas the other two do, the inflexion being more pronounced in the case of the gelatin, which had been boiled.   It has long been known that gelatin, if heated for a length of time above 37° C., gradually passes into a form which has not the power of forming a jelly and its solutions have diminished viscosities.   The transition is more rapid the higher the temperature.   It is therefore essential in glue and gelatin manufacture to avoid this change taking place as much as possible.   The smooth and inflected curves thus obtained account for the different forms of titration curves

obtained by previous workers. The presence of the inflexion appears to be accounted for by some decomposition having taken place, liberating more carboxyl groups, and the fact that the solution prepared from Coignet's gelatin showed the inflexion suggests that it, too, must have contained some decomposition product, probably due to too long heating during the process of its manufacture. The effect of heating gelatin is to produce a soluble form, the transition into which being partly irreversible. Commercial gelatins contain varying proportions of this soluble product, in addition to peptones and other decomposition products. It
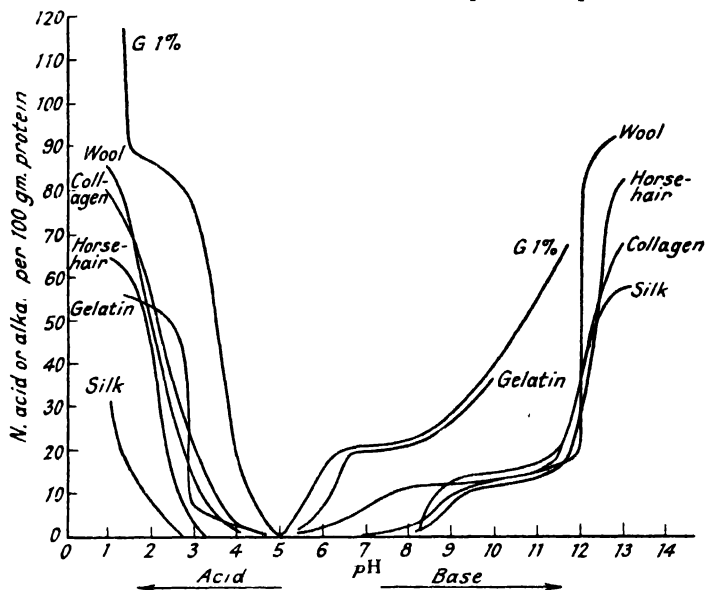
Fig. 163.

is interesting to notice that this observation of the author with gelatin is similar to that of Komatsu and Okinaka (*Bull. Chem. Soc.*, Japan, 1926, 1, 151) in connexion with their studies of the action of superheated water at 120° C. on insoluble proteins, such as edestin, gliadin, and casein. They found that portions thereby became soluble and on titration with sodium hydroxide gave these peculiar inflexions, the magnitude of which depended upon the length of time of heating.

Fig. 163, which is taken from a paper by Lloyd and Bidder, brings out the similarity of the various proteins with solid gelatin. In solution, gelatin, although giving a comparable titration curve, is more reactive than when in the gel form. Curve G 1% is that of a 1% solution of gelatin.

Swelling of Gelatin and the Plumping of Hides.

If gelatin is immersed in solutions of different pH values, it is found that when immersed in solutions at the isoelectric point, *viz.*, pH 4·7, it undergoes the minimum swelling. Lloyd (*Biochem. J.*, 1920, **14**, 147) has investigated the swelling of gelatin in leaf-form by finding the increase in weight per each gram of gelatin. Her results, together with those of Sweet (*vide* Sheppard, *Ind. Eng. Chem.*, 1922, **14**, 1025) are given as broken lines in Fig. 164, the appropriate ordinate being given on the right-hand side. It will be observed that, on the acid side of pH 4·7, both curves showed a considerable absorption of water from solutions, which reached a maximum value in solutions at pH 2·5–2·6. A more gradual swelling occurred on the alkaline side of the isoelectric point.

The isoelectric point of collagen, in the form of hide powder, has been determined. Thomas and Kelly (*J. Amer. Chem. Soc.*, 1922, **44**, 195) obtained a value of pH 5 by means of acid and basic dyes. E. C. Porter (*J.I.S.L.T.C.*, 1921, **5**, 259), however, arrived at a value of pH 4·8 as being the point which caused the minimum swelling of hide powder. The same value, pH 4·7–4·8, is indicated by the titration curves of Atkin and Campos (*loc. cit.*) (*c.f.* Déribéré, *Rev. Mat. Plast.*, 1934, **10**, 363 ; *Koll.-Z.*, 1935, **72**, 249 ; Dulitzkaja and Sokolov, *Koll. Shur.*, 1935, **1**, 417). Highberger (*J.A.L.C.A.*, 1936, **31**, 345) however, considers that collagen has an isoelectric range from pH 4·9 to pH 6·0. It should be mentioned that Porter found points of maximum swelling at pH 2·4 and 12·5. Hence it appears that there is a very close similarity in the physical chemistry of gelatin and its precursor, collagen, and therefore it would be expected that there ought to exist a close analogy between the plumping of hides and the swelling of gelatin. Fig. 164 gives curves which correspond to the plumping of calf skin as determined by Wilson and Gallun (*Ind. Eng. Chem.*, 1923, **15**, 376) by means of a thickness gauge having a plunger with a circular base 1 square centimetre in area and capable of pressing on the skin under constant pressure (*cf.* Wood, Sand, and Law, *J. Soc. Chem. Ind.*, 1912, **31**, 210 ; 1913, **32**, 398), and to the plumping of cow-hide butt by Page and Gilman (*Ind. Eng. Chem.*, 1927, **19**, 251) using a similar method. The latter chemists aimed at following more closely the changes in plumping under actual tannery conditions by using hide which has been soaked, limed, unhaired and fleshed as the standard instead of hide which had only been bated. Page and Gilman's data showing the variation in pH with the amount of

acid (hydrochloric, sulphuric, and lactic) added to hide compare with those given in Fig. 164 for gelatin. The experiments of E. C. Porter (*loc. cit.*) on the swelling of hide powder in solutions of varying *p*H values are of interest in that they also show that there is a close relationship between the swelling of collagen and
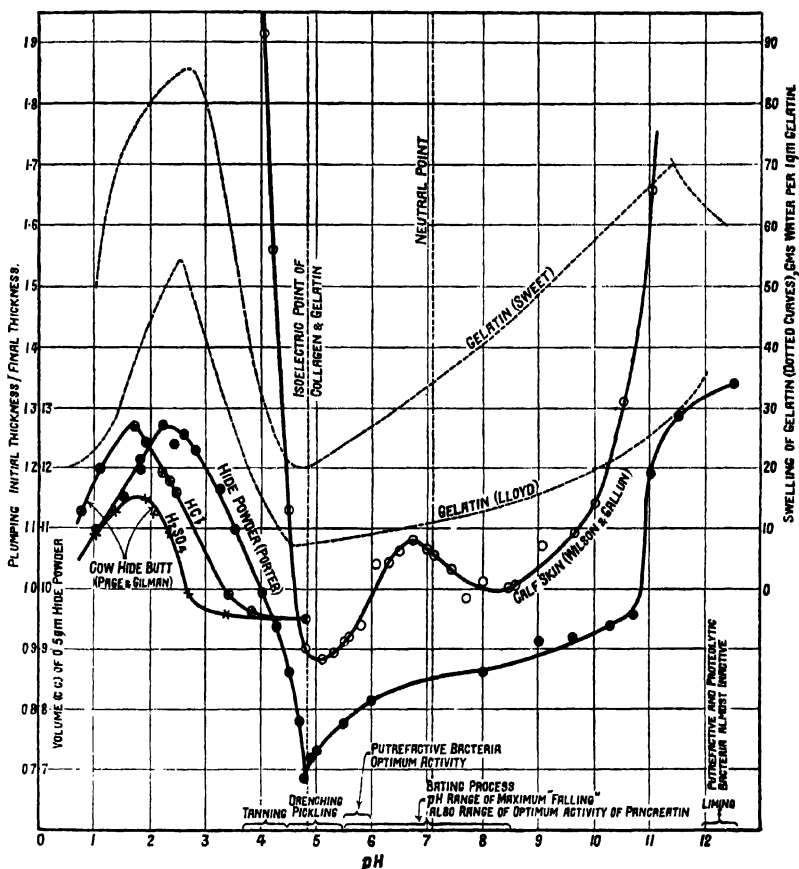
FIG. 164.—Variation in the Degree of Plumping of Hides with the *p*H of Plumping Liquors ; also Variation in the Swelling of Gelatin Immersed in Solutions of different *p*H Values.

of gelatin. He found the volume of hide powder, which had been ground such that it passed through a " 30 " mesh sieve (*i.e.*, a sieve having 30 strands of wire per linear inch) but was retained by a " 60 " sieve, when allowed to swell in different buffer solutions. For this purpose he took o·5 gram of hide powder

and immersed it in 250 c.c. of solution, and after placing in a thermostat for 48 hours with frequent shaking he measured the volume of the swollen powder which had settled down. Such a volume does not represent the true one since a considerable proportion of solution must have been included between the swollen particles, but for comparative purposes this, Porter states, is of no importance. In order to have some check on the repressing effect on the swelling, neutral salts were kept as far as was possible at a constant concentration. R. E. Porter (*J.A.L.C.A.*, 1925, **20**, 282) has also studied the plumping of split and unsplit cowhide. Page and Gilman suggest that the reason why the maximum plumping occurred at pH 1·8, instead of at a higher pH as in the case of gelatin, is to be found in the fact that the pH actually recorded in the hide experiments was that of the external liquor, which most probably was much higher than that which ruled in the interior of the hide. It appears, therefore, that the cause of swelling is in some way related, to the reactivity of gelatin or collagen as either a base or an acid. It is true that swelling can be repressed by the addition of neutral salts to the bath, which is probably best accounted for by the Procter-Wilson application of the Donnan theory of membrane equilibria and not by any suppression of the ionisation of the gelatin salts (Procter and Wilson, *J. Chem. Soc.*, 1916, **109**, 307).

The swelling of collagen fibres, prepared from ox-hide, has been investigated by Lloyd, Marriot and Pleass (*Trans. Faraday Soc.*, 1933, **29**, 554). Maximum increases in volume occur at about pH 2 and at pH 12·0–12·5. Almost constant swelling occurs within the range, pH 5·5–9·0, for fresh fibres and pH 4–10 for dry fibres.

The problem of hydration of gelatin, as apart from that of swelling, has been investigated by Neville, Theis and K'Burg (*Ind. Eng. Chem.*, 1930, **22**, 57, 60) who find that at the isoelectric point the swelling due to hydration is at its maximum. With regard to cured hides, hydration passes through a sharp minimum between pH 3 and 4 and becomes a maximum at about pH 5 (Theis and Neville, *ibid.*, 64, 66).

We shall now consider the chief instances in which hydrogen-ion concentrations provide some means of control of certain stages of leather manufacture. One of the methods used for the preservation of sheep skins, in particular, before de-woolling is to pickle them in solution of a mineral acid (about N/20, either HCl or H_2SO_4) containing salt to the extent of 2 N. It is essential to regulate the plumping, which will be caused by the acid, and also to be careful to remove the acid before proceeding to tan. Pickled

sheep skins are often chrome-tanned without any further treatment. Much of the plumping can be reduced by washing the pickled skins with concentrated brine. Sometimes skins, which come from infected areas (anthrax, foot-and-mouth disease, and rinderpest), require disinfection, and the use of acids in the disinfecting solutions introduces difficulties. A. Seymour-Jones (1910) advocated a method for the eradication of anthrax by immersing the dried skins before transportation from 1 to 3 days in a 1 per cent. solution of formic acid and 0·02 per cent. of mercuric chloride. The swelling is afterwards repressed by soaking the skins for an hour in a saturated solution of common salt. Another method is that of Schattenfroh (*Collegium*, 1911, 248), who disinfects with a 2 per cent. HCl and 10 per cent. NaCl solution at 40° C. for three days. In both cases the acid will tend to plump the skins though this will be largely prevented by the brine. Instead of the usual curing process for packer hides, Benkelaer (*J.A.L.C.A.*, 1938, 33, 470) recommends immersion for 14–20 hours in a saturated solution of salt containing boric acid and borax so as to maintain a pH of 6·8–7·0.

Except in the case of sheep skins, when de-woolling is carried out on skins which have been treated with acid, the most usual way is to prepare them for unhairing by soaking in alkaline solutions. Here great care must be exercised, for if a liquor be used having too high a pH it may cause considerable damage to both the skins and the hair. Alkali, however, has the advantage that, in causing some little decomposition to take place around the roots of the hairs, ammonia is produced, which causes the hair to become loose. Sodium sulphide solutions are often used for this purpose, no doubt because of the buffering effect which sodium sulphide has on the pH in keeping it below that prevailing in free alkali solutions. When caustic soda solutions are used for the preliminary soaking it is essential to use only that concentration which will just promote swelling and at the same time impart to the liquor a reaction of about pH 9–10. After swelling has once been begun the skins are brought to the condition in which they were before drying, by soaking in water.

The use of a saturated solution of slaked lime in the liming process enables a very considerable swelling of the hide to take place and fixes the maximum pH attainable at 12·5. The swollen condition facilitates the enzyme action in the bating process in removing the elastin, and the organic acids so formed cause the pH to fall to about 7·5. This results in the " falling " of the skin, but care must be taken to see that the pH does not become so low as 5·5–6·0, which is the range in which the

putrefactive bacteria become active. Immediately before any of the usual tanning processes can ·be applied the pH has to be brought still lower, and it is this which requires careful control for much of the success or failure of tanning will depend upon it. This is effected by either " drenching " or pickling." For vegetable tanning the liquors are usually below pH 5, and for chrome tanning below pH 4. It is necessary, therefore, to bring the pH below that of the isoelectric point of collagen, pH 4·7.

CHAPTER XXXIV

CHROME TANNING AND OTHER MINERAL TANNING PROCESSES—THE IMPORTANCE OF HYDROGEN-ION CONCENTRATION

OF the several mineral tannages which have been proposed, only those involving the use of basic chromium salt solutions have as yet been adopted to any great extent. Basic alum solutions are sometimes employed for certain types of leathers, and owing to the exigencies of the War Germany was compelled to use iron tannages. Chrome-tanned leathers have many good points which tend to make them superior to vegetable-tanned leathers. In chrome-tanned leather the amount of tanning material is about 5 per cent. of the finished leather as compared with 50 per cent. in the vegetable-tanned leather, and consequently the larger amount of filling, usually grease and wax, required by the former, makes it more durable. On account of their waterproofness and durability chrome leathers are used in the uppers of the better quality boots, in soles, harness, belting and hydraulic leathers. Other mineral tannages have been tried, e.g., titanium salts, tin salts, silicates, and in some cases they have been patented, but it is probable that they have so far not been much used. The metal salts which have passed into general use in the tannery are mainly those of chromium, aluminium, and ferric iron.

The fact that salts of the forgoing metallic bases, which as far as their precipitation pH's are concerned (vide Britton, J. Chem. Soc., 1925, **127**, 2157), appear to be among the weakest, is significant, and so also is the fact that the salt solutions of these particular bases can be rendered appreciably basic by the addition of alkalis or hydrolysing agents before a precipitate begins to appear. This extremely important power of forming " soluble basic salts " has a profound influence upon the reactions of chromium salts (J. Chem. Soc., 1925, **127**, 2120 ; 1926, **125**, 270). Their importance in chrome tanning and the reverse process of extracting (stripping) chromium oxide from leather, thereby rendering leather scrap available for glue manufacture, will be discussed in this chapter and also in Chapter XXXV, which will deal more particularly with chrome liquors and the theory of chrome tanning.

Chrome Tanning.

It was pointed out in the previous chapter that it was advisable to bring the pH of the skin or pelt somewhere near to that of the isoelectric point of collagen. At this point the pelt is more penetrable to tanning liquors than it is when swollen on either the acid or alkaline side of the isoelectric point. To have the pelt in the maximum " fallen " condition is also an advantage as far as chrome tanning is concerned, for this will tend to lessen the " emptiness " of the chrome tannage. There is much controversy, regarding the state of the chrome-tanning liquors, as to whether they should be nearly on the point of precipitation, and whether regulation of their hydrogen-ion concentrations is really necessary. There is, however, no doubt that both these factors do play important parts. Much depends upon the pH of the pelt immediately before tanning and the extent by which it may be removed from the isoelectric point through the acidity of the tanning liquors. The nature of the chrome-tanning bath and the reactions in which the hide substance most probably participates cause hydrogen-ion concentrations to be set up within the skin which are very different from those ruling in the baths. It is generally agreed that pelt tanned whilst in the " fallen " state tends to be soft and pliable, whereas in the swollen state it is often hard and brittle. The swelling which takes place in the chrome bath somewhat impedes tanning, but the rate of tanning is of secondary importance when the quality of leather required is considered. The hydrogen-ion concentration of the tanning liquor is certainly one of the main factors which determine the properties of the resulting leather.

We shall now consider the various types of liquors used in chrome tanning. They fall in one of two categories : (1) one-bath processes, and (2) two-bath processes. Both classes are in effect the same : in the one-bath processes the pelt is immersed in a soluble basic chromium salt solution, usually the sulphate ; and in the two-bath process the pelt is first immersed in a chromic acid solution or an acidified solution of potassium or sodium dichromate, then removed and allowed to stand for some time in the dark, and finally immersed in a solution containing an excess of sodium thiosulphate and carefully regulated amounts of hydrochloric acid. The first practical method was introduced by Knapp in 1858, and involved the use of basic chromium chloride, produced by the addition of sodium hydroxide to a solution of chromium chloride. This process was resuscitated in 1893 by Martin Dennis, who patented the use of a solution of

chromium chloride to which sodium carbonate had been added in an amount insufficient to produce precipitation. Eitner in 1881 employed a solution of basic chromium sulphate of approximately the composition CrOHSO₄ prepared by adding caustic soda to chrome alum. Balderston (*J.A.L.C.A.*, 1924, **19**, 105) prepared the same bath by reducing sodium dichromate with a current of sulphur dioxide, thus :

$$Na_2Cr_2O_7 + 3SO_2 + H_2O \rightarrow 2Cr(OH)SO_4 + Na_2SO_4.$$
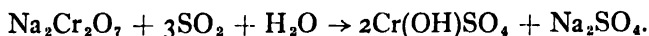
The excess of sulphur dioxide, in giving increased acidity, will have some effect upon the tannage. Other methods of preparing the one-bath tanning liquors from dichromates are employed. A method due to Procter (*Leather Trades Review*, January 12, 1897) brings about the reduction with sugar or other carbohydrates in the presence of such a limited quantity of hydrochloric acid as to produce a basic salt. Thus, a solution may be made by dissolving 3 parts of sodium or potassium dichromate in a convenient amount of water, adding 6 parts by weight of concentrated hydrochloric acid, and then cane sugar or glucose carefully until a green solution is obtained, which may be made up to 100 parts. Such a solution has about the same concentration as that of a 10 per cent. solution of basic chrome alum. Eberle has patented " Chromalin " (D.R.P. 119042/1898, 130678/1899), which is a dichromate reduced with organic substances, *e.g.*, glycerine, glucose sugar, starch. Burton and Glover (B.P. 184360/1921) reduce with tea-dust in hydrochloric or sulphuric acid solutions. Heinzerling (1879) used a solution of potassium dichromate and ordinary alum. The chromic acid fixed suffered reduction by the organic material of the skin. This method was not a commercial success ; it was, in effect, a combined chrome-alumina tannage. Another unsuccessful combined tannage, that of iron and chrome, was advanced by Cavallin, in which the pelt was first impregnated with potassium dichromate solution and reduction subsequently effected by treatment with a solution of ferrous sulphate. This is an example of a two-bath tannage. The first chrome-tanning process to meet with commercial success was that due to Schultz, in which the first bath was acidified potassium dichromate and the second, acidified sodium thiosulphate. Despite the simplicity, ease of control, and efficiency of the one-bath scheme, the Schultz method still finds wide application for the manufacture of both light and heavy leathers. Many modifications of the two kinds of tanning have been patented, the single baths usually containing certain sodium salts—*e.g.*, acetates, formates, etc.—and the double baths differing in the

reducing agent employed, *e.g.*, sulphites of sodium and sulphurous acid solutions of alumina and zinc oxide (*cf.* Hirsch, U.S.P. 1,404,957/1922).

Klanfer and Kenedi (*J..1.L.C.A.*, 1951, **46**, 78) advocate a pre-reduction immersion of the pelt in a bath of sodium thiosulphate, for not only does such a treatment lead to an even distribution of chrome but it raises the pH from 4 to 5 at which the distribution can be effected.

One-Bath Chrome Tanning.

Some experiments by Lumière and Seyewetz (*Bull. Soc. Chim.*, 1903 (3), **29**, 1077) on the action of chromic salt solutions on sheets of gelatin and gelatin sols throw some light on the chrome-tanning action. Chrome alum and most of the normal chromic salts when added in adequate amounts render gelatin insoluble, even in boiling water, and imputrescible. The ratio of chromium to acid radical in the solution before and after treatment was nearly the same, indicating that the chromic salt must have been taken up as such by the gelatin. By repeated washing with boiling water of the gelatin tanned with chromic sulphate, much of the acid radical was removed, the gelatin swelled and some passed into solution. When, however, the gelatin was treated with dilute alkali it was found possible to extract the acid without either causing it to swell or to become soluble. It had previously been found by Namias that the power of chrome alum solution to tan gelatin was increased if alkali were added to it until precipitation was about to begin. Lumière and Seyewetz found that Recoura's green basic sulphate ($2Cr_2O_3,5SO_3$) caused the gelatin to resist repeated washing much more satisfactorily. Procter and Law (*Collegium*, 1909, **326**, 199, 209) studied the diffusion of basic chromium, ferric and aluminium salt solutions into gelatin jellies and found, by observing the movement of a red phenolphthalein boundary, that the acid always diffused into the jellies more quickly than the cation, continually making the salt more and more basic until a part became incapable of further diffusion and then precipitated within the jellies. In time the mother-liquors became more acid, but the precipitates formed in the jellies could be re-dissolved only by means of considerably acid solutions. Stiasny (*Collegium*, 1908, **325**, 337) obtained quantitative evidence of the fact that the ratio of acid radical to chromium in the tanning solution became smaller as the pelt underwent tanning. He experimented upon cubes of butt in chromium sulphate solution and in a basic chromium sulphate solution. Table 203 gives some

TABLE 203

SHOWING VARIATION IN CR : SO₄ IN TANNING LIQUOR AND IN
BASIC SULPHATE FIXED BY PELT

Time after beginning of Tanning.	Original.	15 min.	1 hour.	4 hours.	24 hours.	48 hours.
(a) Chromium Sulphate.						
Parts SO₄ in Liquor . .	146·1	133·3	123·3	118·2	121·7	130·3
Parts SO₄ in Pelt . . .	—	792	449	257	93·4	—
(b) Basic Chromium Sulphate [Cr(OH)₀.₉(SO₄)₁.₁].						
Parts SO₄ in Liquor . .	105·5	100·4	101·2	—	102·1	102·9
Parts SO₄ in Pelt . . .	—	208	92·4	—	89·4	—

of his results, the ratio of acid radical being recorded as parts by
weight of SO_4 combined with 52 parts of chromium (i.e., At. Wt.).

It will be observed that in both cases a very rapid absorption
by the pelt of sulphate occurred, such that the ratios of parts of
Cr : parts SO_4 therein were considerably higher than that, viz.,
144 parts SO_4, required to form the normal chromium sulphate.
The pelt immersed in the normal sulphate solution contained,
however, 93·4 parts SO_4 after 24 hours (i.e., $= Cr_2O_3, 1·93SO_4$),
whereas the other contained 92·4 ($Cr_2O_3, 1·92SO_4$) within an
hour. The sulphate ratio in the normal sulphate solution shows
that the salt first became basic, but as the chromium salt
adsorbed by the pelt became basic, so did the solution become less
basic. More extensive investigations have been made by Thomas
and Kelly (J. Amer. Leather Trades, C.A., 1920, 15, 487) and
Thomas, Baldwin and Kelly (ibid., p. 147) on hide powder over
longer periods. They followed the composition of the tanning
liquor and the powder from time to time and also recorded the
variations in hydrogen-ion concentration of the solutions. The
former workers used 5 grams of hide powder in 200 c.c. of ordinary
chromium sulphate solution containing 16·4 grams of chromium
oxide per litre, and the latter, using the same quantities, employed
as their tanning liquor a stock chrome liquor (Cr_2O_3 215·0 grams
per litre, SO_3 219·0 ; Fe_2O_3 30·9 ; Al_2O_3 3·2 ; and NaCl 6·5)
diluted to 16·98 grams Cr_2O_3 per litre. If the amount of sulphate
in combination with the iron oxide and the alumina be neglected,
it is found that the composition of the basic chromium sulphate
in the solution corresponded with $Cr(OH)_{1·06}(SO_4)_{0·97}$. The tan-
ning solutions are thus approximately the same with respect to
their chromium content and the two series of experiments become

TABLE 204

Tanning Liquor.	Cr$_2$(SO$_4$)$_3$.			Cr(OH)$_{1.06}$(SO$_4$)$_{0.97}$.		
Time.	pH of Liquor.	Composition of Hide Powder.		pH of Liquor.	Composition of Hide Powder.	
		% Cr$_2$O$_3$.	Mols. SO$_3$ 1Cr$_2$O$_3$.		% Cr$_2$O$_3$.	Mols. SO$_3$ 1Cr$_2$O$_3$.
1 hour . . .	2·12	1·5	4·0	3·19	3·5	3·6
2 hours . .	2·09	2·2	3·2	3·14	5·6	2·1
4 „ . . .	2·03	3·8	3·4	3·16	6·9	1·9
6 „ . . .	2·00	4·5	2·1	3·19	7·7	1·9
8 „ . . .	1·97	5·3	2·0	3·20	8·0	1·8
12 „ . . .	1·91	6·3	1·9	3·22	8·6	1·9
1 day . . .	1·95	7·7	1·8	3·26	—	1·7
2 days . .	2·04	8·5	1·8	3·28	10·4	1·7
3 „ . . .	2·08	8·9	1·8	3·25	10·8	1·7
4 „ . . .	2·10	9·2	1·8	3·21	11·0	1·7
8 „ . . .	—	9·9	1·8	—	—	—
16 „ . . .	2·08	10·1	1·9	—	—	—
32 „ . . .	2·11	10·7	1·8	—	—	—
64 „ . . .	—	10·7	1·8	—	—	—

comparable.   The data given in Table 204 were compiled from their results.

This table shows that from tanning solutions of equal chromium content (a) there was an initial increase in pH, but one which was much greater in the ordinary sulphate solution, followed by a gradual increase in pH, (b) the chromium adsorption, and therefore tanning action, was more rapid from the basic solution, (c) the ultimate composition and amounts of the basic chromium sulphate taken up by the hide powder from the two solutions were approximately the same.   The amount of chromium oxide adsorbed from the basic sulphate solutions in 48 hours shows that, in that time, the tanning effected was nearly at a maximum, for very little adsorption took place subsequently.

Hitherto nothing has been said of the effects which may be produced by varying the concentration of tanning liquors, and also the " basic-ness " of the liquors.   These are shown by the curves given in Fig. 165, which illustrate the results obtained by Thomas and Kelly (*Ind. Eng. Chem.*, 1921, **13**, 65), Baldwin (*J. Amer. Leather T.C.A.*, 1919, **14**, 433), and Gustavson and Widen (*Ind. Eng. Chem.*, 1925, **17**, 577) with hide powder.   The curves representing Baldwin's and Thomas and Kelly's data are denoted by their names, the others refer to Gustavson and Widen's work. The compositions of the basic solutes are given in the diagram and also the various pH ranges of the different liquors.   The chrome solutions used by Baldwin, Thomas, and Kelly were apparently impure commercial liquors and their results, therefore,

are not strictly comparable with those of Gustavson and Widen, who took special precautions to prepare pure solutions. Gustavson and Widen record only one series of sulphate contents of their tanned hide substance, obtained from the solutions of 53·5 per cent. " basicity " (*vide infra*), *i.e.*, those corresponding to $Cr(OH)_{1.61}(SO_4)_{0.70}$. The chromium sulphate fixed agreed on the average with $Cr_2O_3, 1.64SO_3$; the variations from these molar proportions being small. Thomas and Kelly's data reveal the
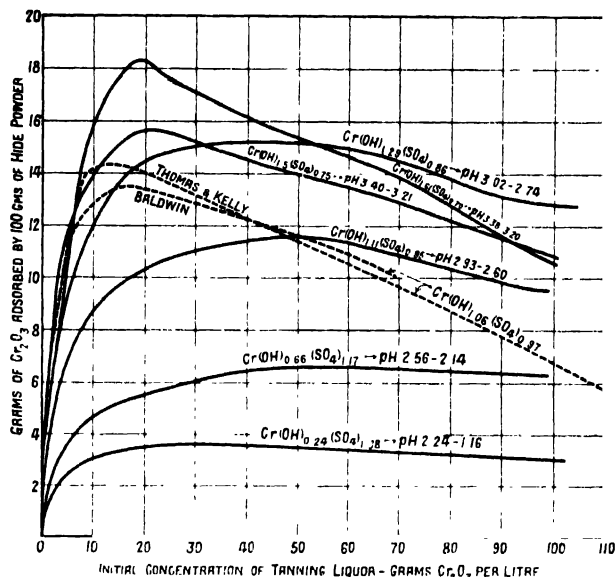
FIG. 165.—Adsorption of Basic Chromium Sulphate by Hide Powder.

fact that the basic chromium sulphate in the powders contained between 1·5 to 1·7 molecules SO_3 to $1Cr_2O_3$, the liquors used for tanning containing up to 73 grams Cr_2O_3 per litre. Thereafter, the sulphate content increased, and in one case exceeded 3 molecules to 1 Cr_2O_3. Baldwin's data indicate more than 2 molecules SO_3 to $1Cr_2O_3$ in the hide substance immersed in the dilute solutions of less than 2 grams Cr_2O_3 per litre; and from 2–25 grams Cr_2O_3 per litre solutions the ratio remained fairly constant at 1·8 molecules, and then increased to 2·5 molecules in the substance with 66·4 grams chrome per litre solution.

The adsorption curves in Fig. 165 show that there are two factors which have considerable influence on the amount of basic chromium sulphate, fixed by hide powder, *viz.*, (1) the degree of " basic-ness " of the chrome liquor, and (2) the concentration of the liquor. The optimum fixation was produced by those solu-

tions which had been rendered basic to the maximum extent. According to the curves of Baldwin, Thomas, and Kelly, it would seem that the most efficient concentrations lay between 10 and 20 grams chromic oxide per litre. From Gustavson and Widen's curves it is seen that from the two most basic solutions—$Cr(OH)_{1.6}$ $(SO_4)_{0.7}$, and $Cr(OH)_{1.5}(SO_4)_{0.75}$—the greatest adsorption occurred when the liquors contained about 20 grams Cr_2O_3 per litre. Whilst the adsorptions, which took place from the less basic solutions of this chromic oxide concentration, had not attained their respective maxima, the increased fixations which accompanied further increases in concentration of the various chrome liquors were not considerable. The curves also show the superiority of chrome liquors in which the chromium sulphate corresponded with $Cr(OH)SO_4$, or were even more basic. It is interesting to note that the pH of the liquors increased as their " basicity " increased, varying from pH 1·16 for the most concentrated solutions of the least basic salts, to pH 3·38 for the least concentrated of the most basic solutions. The hydrogen-ion concentration of those solutions, which produced most efficient tanning, was in the region of pH 3. *They were not, however, buffered at this value, and on the withdrawal of any acid, such as would occur in reacting with collagen, the pH would undergo a sudden increase, and in consequence precipitation within the pelt would eventually ensue.* This, it is believed, is what happens to that liquor which finds its way into the pelt, the fibres of which thereby become tanned. If this be the case, then the pH inside the pelt will be much higher, with its resultant effect on its swelling, than in the external liquor. Hence it is evident that the process of tanning will be largely facilitated by maintaining as high a pH in the external liquor as possible.

The problem of finding some suitable method of expressing the degree of " basic-ness "—technically, though erroneously, termed " basicity "—of chrome liquors has been one of some difficulty. Of the several methods which are used, two have gained general use : (1) to give the number of parts by weight of SO_4 combined with 52 parts of Cr ; thus 144 parts correspond with $Cr_2(SO_4)_3$, 96 parts with $CrOHSO_4$, 48 parts with $Cr(OH)_2(SO_4)_{0.5}$; (2) to express it as the percentage of chromium in combination with basic groups (OH) of the total weight of chromium in combination with both hydroxyl and acid groups, *e.g.*, 33·3 per cent. basicity corresponds to $Cr(OH)SO_4$; 66·7 per cent. to $Cr(OH)_2(SO_4)_{0.5}$ and 0 per cent. with $Cr_2(SO_4)_3$. Though the first method has been widely used in this country and on the Continent, it is rapidly being superseded by the second method.

In order to vary the basicity and hence the stability of chrome tanning liquors so as to obtain some desired quality in the resulting leather, certain acids and salts are sometimes included in the baths. Neutral salts, *e.g.*, the chlorides and sulphates of the alkali metals, bring about a suppression of the swelling of the pelt, and, according to the experiments of Burton and Glover (*J.I.S.L.T.C.*, 1922, **6**, 6), on the action of basic chromium sulphate solutions on calf skin, ox-hide and cow-hide, they retard the penetration of chromium into the pelt. This retardation was greater with both sodium and potassium sulphates than with sodium chloride, though it should be mentioned that the amounts of sulphate fixed by the pelt in presence of sodium chloride were initially greater, but tended to become equal after very protracted periods of immersion (about 90 days). Their results, concerning the influence which the basicity of the chrome liquor has on the rate of tanning, *viz.*, the greater the basicity the greater the speed at which chrome adsorption proceeds, are in accord with those given by hide powder. Burton and Glover (*ibid.*, 1921, **5**, 183) obtained analogous results with gelatin. Other substances are sometimes put into, or are developed in, the chrome baths, *e.g.*, acetates, formates, hydroxy-compounds, oxalates, sulphites, in order to modify their tanning action either by bringing the *p*H of the liquors nearer to the isoelectric *p*H of collagen, or, by making precipitation of basic chrome salts more difficult. The effects thus obtained will be discussed in the next chapter.

Neutralisation of Chrome-Tanned Leather. Fat Liquoring.

It will be inferred from Tables 203 and 204 that the chrome substance fixed by leather has the molecular proportions of an indefinite basic salt. Some of the acid radical on coming into contact with water becomes hydrolysable, and in order that the leather shall not deteriorate, and that fatty acids shall not be precipitated and so produce unsatisfactory surfaces when the leather is subjected to the " fat-liquoring " process, it is essential to neutralise to about *p*H 6 after tanning. Fat-liquoring should be carried out immediately afterwards so that the acid in the interior of the leather will not have had time to reach the surface. This acid, however, will be neutralised as soon as the fat-liquor penetrates through the leather. Over-neutralisation will decompose the basic chrome salt, and besides impairing the appearance of the leather, will reduce its tensile strength and give a hard " tinny " leather. The decomposition of the fat-liquor through under-neutralisation will impart to the leather a rough surface, and there will be a pronounced tendency for the leather to crack on drying

(Procter and Griffith, *J.A.L.C.A.*, 1917, 612; Burton, *J.I.S.L.T.C.* 1922, **6**, 160). Stiasny's mixture (*Collegium*, 1912, **11**, 293) is regarded as a perfectly safe neutralising agent, in that it cannot lead to over-neutralisation. It comprises a 2 per cent. Na_2CO_3 solution containing 2 per cent., or more if necessary, of ammonium chloride or sulphate. In this case the liberated carbon dioxide and the ammonium salt both exert a buffering action and prevent the pH from rising too high. Sodium bicarbonate and borax are among the safest neutralising agents, though should they be added in excess, the grain dries to a horny surface. Eitner advocated sodium silicate, but this has the disadvantage, if used in excess, of causing the deposition of too much colloidal silica on the hide fibres, thus producing a brittle leather. With sodium thiosulphate, even when added in excess, there can be no possibility of over-neutralising, and this is also true with sodium phosphate, Na_2HPO_4, for both automatically regulate the pH to a suitable value. The former sets sulphur free, which affects the colour of the leather, and the latter replaces some of the sulphate (or chloride) in the leather by phosphate to produce a fuller leather. Chrome sole leathers are not usually fat-liquored, and sometimes not even neutralised, but are dried out and impregnated with a mixture of melted waxes and rosin, which give firmness and water-resistance.

Both the pH of the skin and of the fat-liquor are of importance, so also is the inclusion of a fat emulsifier in the fat-liquor. By raising the pH of the skin the amount of oil taken up steadily increases until pH 4 is attained. Thereafter, it decreases. Theis and Hunt (*Ind. Eng. Chem.*, 1931, **23**, 50; 1932, **24**, 799) state that skins of pH below 5 have a greasy feel, but above pH 5 the feel becomes soft and silky, and between pH 7 and pH 9 the skins are well-lubricated and well-liquored. J. A. Wilson (*J.A.L.C.A.*, 1937, **32**, 578) begins fat-liquoring at pH 6·0 and slowly adds sulphuric acid to pH 3·5–3·7.

Other Mineral Tannages.

Tanning, or " tawing," with alum and sodium chloride solutions, the latter being used to reduce swelling, and the alum very often made basic, is resorted to in the manufacture of glove leather, and also for the preservation of the skins of fur and hair rugs. After the skins have been rubbed with a mixture of egg-yolk, cotton-seed oil, and flour, they are aged for considerable periods, when the precipitated basic aluminium sulphate becomes difficultly soluble, and so tends to become fixed. Then the excess of salt is removed by soaking, and the leather finished as desired.

Solutions containing aluminium sulphate and sodium acetate in molecular proportions have been used for tanning leather within the pH range 3·8–4·8, and leather, suitable for insoles, containing 4 per cent. of alumina has been produced.

According to E. O. Wilson, Reng and Li (*J.A.L.C.A.*, 1935, **30**, 184) the maximum fixation from solutions of sodium aluminium oxalate occurs at pH 5 and from sodium aluminium tartrate at pH 4.

Iron-tanning, by means of basic ferric salts, though it has had some considerable application, cannot be considered satisfactory. The basic ferric salt deposited in the leather in time becomes reduced to the ferrous state by the leather itself, which as a consequence undergoes slow oxidation and so deteriorates. Another disadvantage is the extreme difficulty in neutralising the leather, for on neutralisation the iron salt becomes colloidally dispersed and is washed out of the leather (Jettmar, *Cuir*, 1919, **8**, 106). Iron-tanned leathers are decomposed, and become tender, by water (Moeller, *Z. Leder u. Gerberei Chem.*, 1922, **1**, 166).

M. C. Lamb (F.P. 327945/1902) patented the use of basic solutions of titanic salts, *e.g.*, the basic sulphate, chloride, and oxalate, and pointed out that both tanning and dyeing, the deposited titanium basic salt acting as a mordant, could be effected simultaneously.

Hough (*Cuir*, 1919, 209, 257, and 314) has shown that good leathers can be obtained by tanning with silica by immersing in a 30 per cent. solution of hydrochloric acid, into which a 30 per cent. solution of sodium silicate is poured until the free acid is decinormal. Swelling is kept down by adding salt to the bath. Adding the reactants in the opposite manner leads to unsatisfactory tanning.

Other salts which are stated to have tanning action are those of the rare earths, tin, zinc, thorium, zirconium, and beryllium (Parenzo, *Collegium*, 1910, 121 ; Zacharias, *C.B.*, 1903, **2**, 536; Jettmar, *Chromgerbung*, Leipzig, 1924, 28). Salt solutions of many of these metals can be rendered appreciably basic before the respective hydroxides begin to precipitate. According to Schachowskoy and Frölich (*Kolloid Z.*, 1941, **97**, 336) zirconium salts may produce two types of tannage : (i) a " salt " tannage, (ii) a hydroxide tannage. Type (i) is exhibited by zirconium sulphate solutions from which basic zirconium sulphate is deposited within the pelt at a maximum between pH 2 and 3 (see page 82), and type (ii) takes place from zirconium chloride and nitrate solutions between pH 5 and 6 (see page 79).

CHAPTER XXXV

THE IMPORTANCE OF THE HYDROGEN-ION CONCENTRA-
TION OF CHROME TANNING LIQUORS

To a great extent the quality of chrome leathers is a question of the chrome liquors used in the manufacture. This chapter deals with the modes by which the tanning properties of chrome solutions may be varied. It should be mentioned that the salts of tervalent chromium exhibit in a unique way the phenomenon of " soluble basic salt " formation, on which the process of tanning very largely depends. In connexion with some researches on the pH's at which various hydroxides becomes precipitable (*J. Chem. Soc.*, 1925, **127**, 2127) the author observed that from a very dilute solution of ordinary chrome alum (*i.e.*, violet) precipitation did not begin until 1·0 equivalent of NaOH had been added for each atom of Cr present when a pH 5·3 had been attained, and for precipitation from an ordinary chromium chloride solution 1·07 equivalents of alkali were necessary, the pH then being 5·28. It would seem that soluble basic salts were formed having approximately the formula $Cr(OH)R_2$, where $R = Cl$ or $\frac{1}{2}SO_4$ (see p. 260).

Fig. 166 gives the precipitation curve of violet chrome alum, starting at a pH of 3·2, which indicates that the combined sulphuric acid had become hydrolysed to the extent of 2·2 per cent., and showing a rapid pH increase during the addition of the first equivalent of alkali. The figures on the various curves denote the number of equivalents of alkali. The ordinary chromium chloride curve is exactly similar. If, however, chromium salts are boiled, cooled, and treated with alkali it will be found that more alkali than is the case with an unboiled solution has to be added before precipitation can ensue. The solutions also change in colour, becoming green, when considerable amounts of acid are hydrolysed. Thus, in the author's experiments five minutes' boiling produced in a chromium chloride solution an increase in hydrolysis from 1·6 per cent. before boiling to 16·2 per cent. after boiling, and in the case of chrome alum from 2·2 to 28·7 per cent. The precipitation, in the cold, of the chloride as silver chloride from green chromium chloride solutions, and of the sulphate as barium sulphate from chromium sulphate and chrome alum solutions is far from complete. The proportion

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of chloride precipitated depends upon the silver salt used (whether it contains the radical of weak or of a strong acid), the acid present and the temperature.

The alkali precipitation curve for chrome alum is given in Fig. 166, from which it will be seen that the change in *p*H, unlike
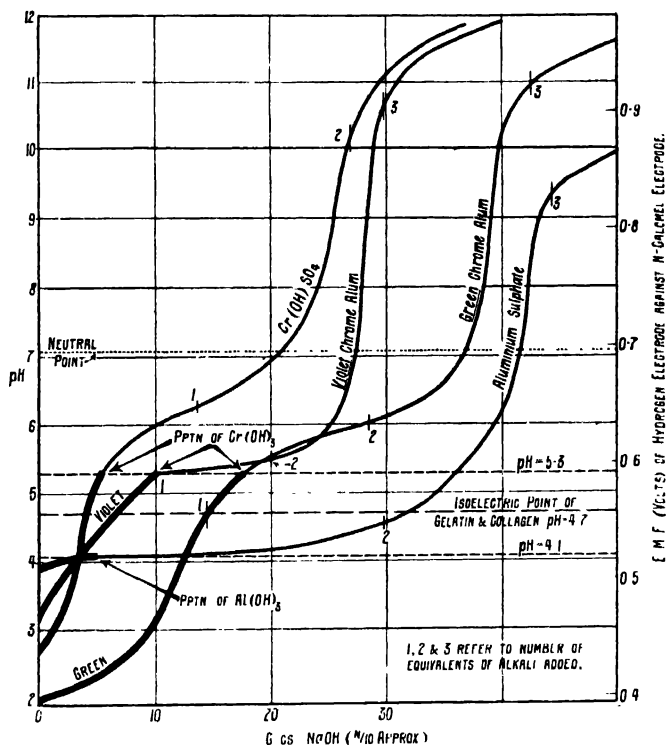
FIG. 166.—Precipitation Curve of Chrome Alum.

the almost rectilinear change produced by the violet chrome alum solution, undergone prior to precipitation is similar to that of neutralisation of an acid. Precipitation began with 1·2 equivalents, whereas it did not occur from the green chloride solution until 1·4 equivalents of alkali had been added.

It is interesting to recall that the tanning powers of the green solutions are less than those of the corresponding violet or blue solutions, due evidently to the greatly increased acidities, *i.e.*, lower *p*H's. Thus, Burton (*J.I.S.L.T.C.*, 1918, **2**, 205) points out that violet chrome alum solutions tan more rapidly than do the green solutions. The exponents of Werner's co-ordination

theory try to account for the change from the violet salt to the green state by a change in molecular orientation, *e.g.*, $[Cr(H_2O)_6]Cl_3 \rightleftharpoons [Cr(H_2O)_4Cl_2]Cl,2H_2O$ but in the opinion of the author it appears that no satisfactory and unequivocal evidence has yet been brought forward to support such a contention. There is very strong evidence that the green solutions correspond to the border line condition between that of true solution and colloidal solution, and they are perhaps best regarded as a form of colloidal electrolyte. This view is incidentally one which helps to provide an explanation of chrome tanning.

As the Werner Theory has been accepted by such well-known leather chemists as Stiasny and Gustavson, it is perhaps desirable to point out here some of the evidence on which Werner based its application to chromium chloride solutions, especially as hydrogen-ion concentration measurements tend to lead to another explanation.

Werner and Gubser (*Ber.*, 1901, **34**, 1579) first applied the theory to chromium chloride, and Lamb and Fonda (*J. Amer. Chem. Soc.*, 1921, **43**, 1154) referred to its application to chromium salts as " perhaps the most striking exemplification of the Werner theory of molecular structure." It is therefore surprising that the evidence, on which Werner and Gubser based their views, is quite unconvincing, and indeed, the difference between the green and violet might well be due to the existence in the green solutions of basic aggregates which are essentially colloidal in nature. The low conductivity of solutions of the green form of chromium chloride was regarded as evidence of the dissociation of a binary salt, $(CrCl_2,4H_2O)Cl,2H_2O$. The abnormal molecular weights calculated from the depression of the freezing-point were supposed to supply fundamental evidence for this structure of the green form, for they happened to be of the order of one-half the molecular weight of hexahydrated chromium chloride. It is strange that the weight of six molecules of water should have been included in the latter molecular weight, seeing that four molecules only are supposed to be present in the nucleus of the complex chromium cation. The observed molecular weights of the violet chromium chloride were of the order of one-quarter of that of the hexahydrated salt, and this was taken as being due to $(Cr6H_2O)Cl_3$. The results show, however, that the observed molecular weights of the violet chloride in the more dilute solutions are somewhat too high—this may be regarded as due to incomplete ionisation—but it is remarkable to find that the agreement between the observed and the theoretical values only becomes perfect for a 12 per cent. solution, in which the dissociation must be far from

complete. Werner and Gubser tried to confirm the view that only one chlorine atom in the green form was ionisable and therefore precipitable with silver nitrate, but they always found that the amounts precipitated were greater than corresponded to one atom, even in rapid estimations carried out at 0°. Similar observations have also been made on the incomplete precipitation with barium chloride from green chromium sulphate solutions. It is difficult to reconcile with the co-ordination theory the observations of Weinland and Koch (*Z. anorg. Chem.*, 1904, **39**, 296) on the precipitability of chlorine from green chromium chloride solutions with various silver salts, both in presence and in absence of free acid. The amount of chlorine precipitated depended on the nature and the quantity of the particular silver salt used ; without the addition of acids, all the silver salts precipitated at least two-thirds of the chloride. The presence of nitric acid had the effect of diminishing the amount of chloride liberated, whereas the silver salts of weak acids, such as acetic, lactic, and nitrous, and silver sulphate immediately precipitated all the chloride. Silver salts of strong acids did not cause complete precipitation and free strong acids suppressed the precipitation even more. Lamb (*J. Amer. Chem. Soc.*, 1906, **28**, 1710 ; Lamb and Fonda, *ibid.*, 1921, **43**, 1154) tried to explain the above observations by a gradual transition from the green variety to the violet due to the hydrogen-ion concentrations ruling during the reactions, but in order to show how the transformation took place they found it necessary to postulate further that the green variety first underwent hydrolysis to form some such basic complex as $CrCl_2OH$.

Precipitation with alkali from both the violet and green forms is dependent on the attainment of a hydrion concentration of about *p*H 5·3. It begins from those solutions which contain chromium in the normal condition when about one equivalent of sodium hydroxide has been added, whilst the green solutions do not yield precipitates until somewhat larger proportions of alkali have been added. The greater amounts of alkali required in the latter case show that the change produced in the solutions on turning from violet or blue to green has rendered the chromium salts more resistant in their behaviour towards alkali.

It is probable that the basic chromium complexes which seem to be present in green solutions are " micellar " in structure and constitute a colloidal electrolyte in which the cations are composed of chromium hydroxide and varying amounts of acid radical, a portion only being ionisable. This would account for the slowness with which silver chloride and barium sulphate may be precipitated from the appropriate green solutions, and this is especially

so when the chromium solutions happen to be basic, such as may be prepared from the basic glassy masses obtained by evaporating solutions of chromium salts to dryness. There appears to be a tendency for one-third of the combined acid in a chromium salt, *i.e.*, the amount corresponding to that which seems to be loosely combined and gives rise to the formation of the " soluble basic salt," to be driven off on evaporation. Thus a basic salt prepared in this way had a composition corresponding to $Cr(OH)SO_4$ and gave in solution no precipitate with barium chloride ; neither did it do so with ammonia except on boiling or keeping. The soluble basic complexes in the green solutions have some properties in common with chromium hydroxide. Chromium hydroxide, which has been suspended in water and boiled, or has been allowed to stand, becomes difficultly soluble in acids, as is also the case with ferric hydroxide, slowly dissolving only in concentrated acid solutions. Hence it is evident why the acids present in Weinland and Koch's experiments did not immediately decompose the green salt and render the chloride available for precipitation, and why the acid actually retarded the precipitation by depressing the ionisation of the colloidal electrolyte. The conception of basic aggregates also supplies an explanation why it was only the silver salts of weak acids which caused the silver chloride to be precipitated. The first reaction taking place between the precipitant and the colloidal electrolyte is one of double decomposition, whereby the chloride anion of the chromium complex is replaced by the anion of a weak acid. This would diminish the hydrogen-ion concentration of the solution, which would therefore tend to approach the value requisite for the precipitation of chromium hydroxide ; the basic complexes would thus be rendered so unstable that the chloride radicals in them would become susceptible to reaction with the silver salt.

Other properties which accompany the change in colour from violet to green in solutions of chromium salts are : (1) increase in conductivity without any comparable change in cryoscopic measurements ; (2) increase in volume of the solutions ; (3) on dialysing green sulphate solutions the liquid in the dialyser becomes increasingly basic whereas the violet salts pass through as such ; (4) green salts are much more occluded by precipitates ; (5) absorption spectra of green solutions are similar to that produced by colloidal chromium hydroxide ; (6) electrical migration experiments of green solutions are unconvincing as far as any possible complex formation is concerned. It appears highly probable that green chromium salt solutions contain some chromium hydroxide in the colloidal condition, which view seems

to be supported by the viscosity data of Partington and Tweedy (*Nature*, March 20, 1926) of solutions of the violet and green chromium chloride. They found that the viscosities of the violet solutions were higher than those of the corresponding green solutions. This is, as would be expected, the lower viscosities of green solutions being caused by the appreciable amounts of hydrochloric acid set free by hydrolysis and the colloidal nature of the basic chloride present in the solutions. As is well known, the viscosity of metallic oxide hydrosols is usually but little greater than that of water, which very probably is also true of hydrosols of basic chromium chloride (*vide* Yeo and Freyer, *J. Phys. Chem.*, 1926, **30**, 1389—these workers also found that the viscosity of basic chromium chloride hydrosols was affected by their *p*H). The curve in Fig. 166 marked $Cr(OH)SO_4$, corresponds to a solution prepared by reducing a solution (100 c.c.) of potassium dichromate with sulphur dioxide and boiling until any excess of gas had been expelled. The *p*H 2·7 of this solution compares with those of basic chrome liquors, and is remarkably lower than that attained, *p*H 5·3, when the violet chrome alum had attained such a " basicity " and was on the point of precipitation. Barium chloride gave a partial precipitation from this solution, suggesting that some sulphate had become locked up by the colloidal aggregates. This solution did not yield a precipitate with alkali until *p*H 5·3 was reached. The solution then corresponded with $Cr(OH)_{1.4}(SO_4)_{0.8}$. *It is an interesting fact that the two elements whose salts should have gained importance as tanning agents are chromium and aluminium, for it happens that the precipitation pH's of their hydroxides are very close to that of the isoelectric point of collagen, pH 4·8 ; pH of $Cr(OH)_3$ 5·3 ; pH of $Al(OH)_3$ 4·2.* Ferric salts on being rendered basic become colloidal in strongly acid solutions, and coagulate in the region of true neutrality (Britton, *J. Chem. Soc.*, 1925, **127**, 2152). Titanic salts which have been patented as tanning agents by Lamb (French P. 327,945), and also used for leather mordanting purposes, on being made basic pass through a colloidal solution stage and precipitate, like ferric hydroxide, when almost the stoicheiometrical amount of alkali has been added commencing at about *p*H 2·3.

The ready hydrolysis which takes place even in strongly basic chromic sulphate solutions causes their *p*H's to be relatively low. Thus Thomas and Baldwin (*J.A.L.T.C.A.*, 1918, **13**, 192) found that a commercial tanning liquor corresponding to $Cr(OH)_{1.2}(SO_4)_{0.88}$ and containing 231 grams Cr_2O_3 per litre had a *p*H of 2·31, but on dilution gave higher *p*H's, 3·0-3·6, for dilutions from 10 to 800, and these *p*H's became slightly higher

after standing for a week, the basic sulphate having therefore become less hydrolysed. They examined the pH of basic sulphate solutions containing 13·86 grams Cr_2O_3 per litre, which had varying basicities after standing for 2 and for 50 days. They found that the more basic solutions, $Cr(OH)_{1.28}(SO_4)_{0.86}$ to $Cr(OH)_{1.6}(SO_4)_{0.7}$, hydrolysed, for they gave initially higher pH's, 3·35–4·27, fell after 2 days to pH 3·35–3·60 but underwent very little further change in 50 days. The less basic solutions, $Cr(OH)_{1.28}(SO_4)_{0.86}$ to $Cr(OH)_{0.7}(SO_4)_{1.15}$ however, underwent the reverse change and increased in pH, from pH 3·2–1·7 to pH 3·3–2·5 after 2 days and to pH 3·3–2·9 after 50 days.

The introduction of the idea of *Precipitation Figures of Chrome Liquors* by McCandlish (*J.I.S.L.T.C.*, 1917, 114) furnishes a useful means for characterising the tanning properties of a liquor. These figures are obtained by titrating 10 c.c. of clear liquor, after previous clarification with kaolin, with a $N/10$ or $N/20$-solution of an alkali. The precipitation point marks the limit to which chrome liquors can be rendered basic. Though solutions that are on the point of precipitation are not without tanning action, they cause an irregular deposition of the basic chromium salt in the pelt. Hence there will be a pronounced tendency for the coarse external layers of chrome to prevent the chrome liquors from penetrating into the interior of the pelt. It is found in practice that *the smaller the Precipitation Figure the greater will be the speed at which tanning will proceed*. Liquors, however, which have very small precipitation numbers very often lead to unsuccessful tanning, due to the rapid reaction of the free acid with the protein of the pelt and the resulting rapid separation of the basic chromium precipitate. The whole liquor may even become turbid. To avoid the possibility of the interior parts of the hide not becoming tanned, it is better to begin the tanning process by using a liquor from which the chrome does not precipitate to any great extent until after the liquor has had time to soak thoroughly into the skin. This may be accomplished by giving a preliminary tannage with a liquor having a high precipitation number, or, having regard to most suitable pH of the pelt during tanning, resort may be made to liquors from which precipitation has been retarded by the presence of such substances as oxalates, acetates, sulphites (*vide infra*, Stiasny). Burton, Wood, and Glover (*J.I.S.L.T.C.*, 1923, 7, 37) have studied the variation in precipitation figures and the pH's of violet and green chrome alum solutions (the latter produced by boiling) with increasing salt concentration. Table 205 has been calculated from their results :—

TABLE 205

PRECIPITATION FIGURES

Gms. of Chrome Alum per Litre.	Violet.			Green.		
	pH.	Pptn. fig. c.c. NaOH for complete pptn	Equivs. OH to 1 Cr.	pH.	Pptn. fig. c.c. NaOH for complete pptn.	Equivs. OH to 1 Cr.
5	3·08	0·33	1·00	2·12	0·50	1·50
10	3·08	0·29	0·87	2·03	0·47	1·41
25	2·99	0·27	0·81	1·86	0·44	1·32
50	2·91	0·26	0·78	1·69	0·41	1·23
75	2·82	0·26	0·78	1·60	0·38	1·14
100	2·73	0·26	0·78	1·52	0·39	1·17

The difference in pH of the violet and green solutions compare well with those given in Fig. 166. The ratios given in the third and sixth columns become, when expressed as percentages, instead of fractions, the basicity numbers of the basic solutions that are on the point of precipitation. The table shows that, whereas the violet solutions may be rendered basic to the extent indicated by $Cr(OH)SO_4$ in dilute solutions, the extent diminishes to $Cr(OH)_{0.78}(SO_4)_{1.11}$ in the concentrated solutions. Green solutions varied from $Cr(OH)_{1.5}(SO_4)_{0.75}$ to $Cr(OH)_{1.17}(SO_4)_{0.91}$. These basic solutions compare with the types of solutions used for tanning. The precipitation figures of violet solutions slowly increase on ageing. When chrome liquors are prepared by reduction of chromic acid or dichromates, it is found that the reducing agent used and the mode in which the reduction is carried out has some effect on the precipitation figure, even though the basicities of the several solutions may be the same. Neutral salts present in the liquors may have great effect on the precipitation figures (cf. Wilson and Kern, J.A.L.C.A., 1917, 12, 445), their effect being, in general, to increase them. This is especially so with sodium chloride, very probably through the conversion of some basic sulphate into basic chloride, which in the case of the green variety causes precipitation to be delayed still further.

Sodium salts of organic acids have an exceptional influence upon chromium salt solutions. When first added they generally delay the precipitation with alkali, the extent of which depends on such factors as ageing or boiling of the solution, and they may even, if added in sufficient quantities, prevent precipitation altogether from taking place. This is true of acetates, oxalates, tartrates, citrates, and sulphites. In a similar fashion, chromium

acetate and oxalate solutions may become on standing or after boiling not precipitable with alkali, and when precipitation does take place from solutions containing one of these salts in an inadequate amount to prevent all precipitation, it is far from complete. It is not surprising, therefore, that both the solutions may in extreme circumstances be incapable of tanning, whereas in general their tanning action is considerably reduced.

The addition of sodium acetate to green chrome alum solution has been found by Burton (*J.A.L.C.A.*, 1923, **18**, 358) to raise the precipitation figure when first added, but after a short time if an adequate amount has been used, to make it infinite, in other words, to prevent precipitation with alkali and hydrolysing agents. He concludes that sodium acetate does not improve tanning, but cites numerous recent patents protecting chrome liquors in which acetates are present. The author's studies (*J. Chem. Soc.*, 1926, 269) throw some light on the nature of the reactions which take place when these sodium salts are added to chromium salt solutions, and from the evidence obtained, he postulated the formation of somewhat stable but soluble basic aggregates, existing very probably in the form of colloidal electrolytes. Fig. 167 contains some pH curves which show the variation in hydrogen-ion concentration produced when approximately decinormal sodium hydroxide was added at $18°$ C. to chrome alum solutions to which either sodium acetate, or oxalate, or tartrate had been previously added. They are of especial interest here in that they show how deeply seated may be the influence which these salts may have in either impeding or preventing precipitation from chromium salt solutions when reacted upon with alkalis. They also explain why small quantities reduce the tanning power of the chrome liquors, whereas when added in larger amounts they render the liquors useless for tanning. It therefore becomes apparent why concentrated solutions of sodium acetate, oxalate, or tartrate are capable of dissolving chromium oxide, and why these solutions may be used as agents for stripping chromed leather, leaving the collagen for subsequent conversion into glue or gelatin. The speed at which dissolution takes place is largely determined by the amount of ageing which the chromium oxide has undergone. The curve corresponding to the titration of 100 c.c. M/100-chrome alum with N/10-NaOH is given in Fig. 167 for purposes of comparison. The curve marked acetate is that of 100 c.c. M/100-chrome alum containing twice the stoicheiometrical amount (*i.e.*, 12 molecules to 1 molecule of chrome alum) of sodium acetate, boiled for about five minutes, cooled to $18°$ C. and 0·0900 N-NaOH added in presence of the hydrogen electrode.

This solution was red, contained the chromium in a basic state, and gave no precipitate with alkali. A similarly prepared solution, but unboiled, was precipitable. The theoretical amount of alkali was 66·7 c.c. The shape and position of the greater part of the curve is very similar to that of free acetic acid, as would be
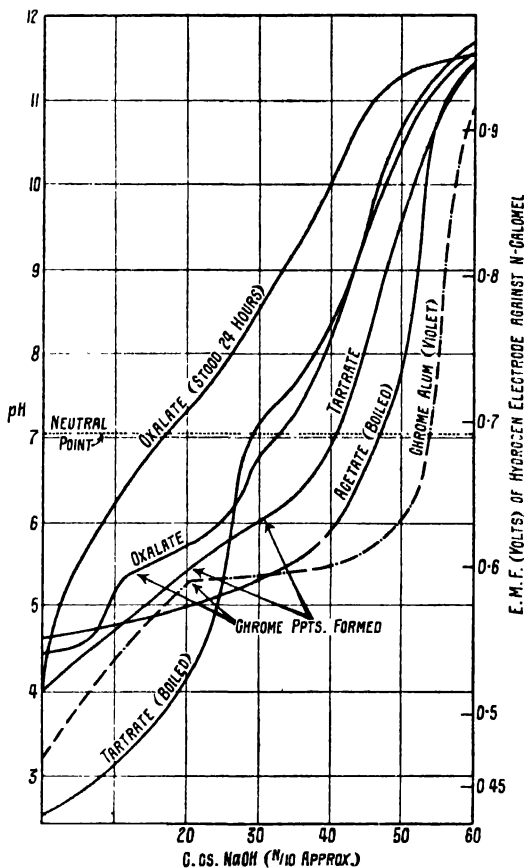
FIG. 167.—Addition of N/10 NaOH Solution to Chrome Alum Solutions containing Acetate, Tartrate, etc.

expected to be the case if the chromium were present in the solution in a basic state and much of the acetic acid had become hydrolysed (see *J. Chem. Soc.*, 1926, 275). The two oxalate curves refer to the action of 0·1082 N-NaOH on 100 c.c. M/100-chrome alum to which 60 c.c. M/10-$Na_2C_2O_4$ had been added. One had stood 24 hours at room temperature, in which time the

solution became non-precipitable, whereas the other solution was titrated immediately and gave a precipitate with 12·5 c.c. of alkali (basicity of solution then being 22·5 per cent.) at pH 5·4. (*N.B.*—pH Cr(OH)$_3$ is 5·3.) The precipitation was partial. The curves show surprisingly higher pH's than were given during a simple precipitation reaction. The same alkali was used in the tartrate titrations. Both solutions contained 100 c.c. M/100-chrome alum and 30 c.c. M/10-sodium tartrate. One was boiled for five minutes and thus rendered non-precipitable with alkali. It was cooled to 18° C. and was red in colour but became green as the alkali was added. The unboiled solution gave a cloudiness with 20·2 c.c. of alkali (basicity = 36·4 per cent., pH 5·4), and the precipitate began to separate with 30·6 c.c. (basicity = 55·1 per cent., pH 6·5). Chromium tartrate solutions themselves are not precipitated with alkali ; neither are those chromium salt solutions to which sodium tartrate has been added in sufficient amounts. There is a risk that in chrome liquors made by reducing with organic matter (sugar, sawdust, etc.) organic acids may be formed, and these will have some effect on the tanning properties of the solution. Procter in his book on Leather Manufacture (1922, p. 265) called attention to the fact that *violet* solutions produced by the reducing with sugar should be avoided on account of their unsatisfactory tanning properties. The salts of these weak organic acids in basic chrome liquors would cause the liquors to assume pH's nearer to that of the isoelectric point of collagen, and in so doing would keep the swelling of the pelt at a minimum and thereby give rise to a softer and fuller leather. Procter and Wilson (*J. Soc. Chem. Ind.*, 1916, **35**, 156) found that solutions of Rochelle salt (potassium sodium tartrate), sodium citrate, and sodium lactate, if used in suitable concentrations, could be used to extract the chrome from tanned leather. H. G. Bennett ("Animal Proteins," p. 135) has also shown that the oxalates and acetates of sodium, potassium, and ammonium have some stripping power.

Dyeing of Chrome Leather.

The pH of chrome leather ranges from 5 to 7 superficially, and from 3·8 to 5 internally. The chief factors which govern successful dyeing are : (i) neutralisation of the leather, (ii) the internal pH, (iii) the pH of the dye-bath, (iv) penetration and diffusion and (v) dispersion of the dyestuff. Elöd (*Collegium*, 1935, 1) considers that the dyeing of chrome leather can only be achieved with highly dispersed dyestuffs ("direct dyestuffs") or by allowing the dye to diffuse into the leather from an alkaline

bath, about *p*H 9, followed by immersion in acid bath at about *p*H 2·5. Maximum combination of the hide substance with the free dye then occurs. (See also Otto, *Angew. Chem.*, 1936, **49**, 175 ; *Collegium*, 1935, 371 ; Herfeld, *Farben. Chem.*, 1936, **7**, 11, 54, 127, 165 ; Burton, *J.S.L.T.C.*, 1936, **20**, 451.)

The Theory of Chrome Tanning, etc.

Perhaps the explanation suggested by Wilson (*J.A.L.C.A.*, 1917, **12**, 114) marks the first step in accounting for chrome tanning as the result of chemical combination. In the absence of a better theory, he sees no objection to considering alum, chrome, and iron leathers as the collagen salts of triacid bases, though he states that in actual tanning there is probably first a fixation of basic salts, and to some extent a fixation of metallic hydroxide upon the hide fibres. The change which accompanies " ageing " of mineral-tanned leathers is probably due to the slow combination between the collagen and the metallic hydroxide precipitated upon the fibres, thus

$$3R{\overset{NH}{\underset{CO}{\Big<}}} + Cr(OH)_3 \rightleftharpoons Cr(NH_2 . R . COO)_3$$

Collagen.   Chrome leather.
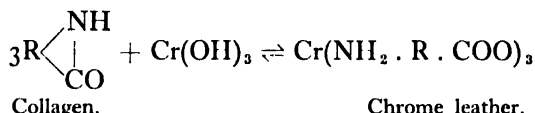
If collagen could be regarded as the anhydride of gelatin, through the extraction of one molecule of water from each molecule, and taking Wilson's value of the molecular weight of gelatin as 768, then that of collagen would be 750. (These figures are very unreliable for the apparent molecular weight is extremely high.) Using this value, it is found that according to the above equation, 100 grams of collagen should combine with 3·38 grams of chromic oxide to form chromium tricollagenate, and 100 grams of gelatin should require 3·30 grams to form chromium trigelatinate. Lamb and Harvey (*Collegium*, London, 1916, 201) state that leather containing 2·8–3·0 per cent. Cr_2O_3 was undertanned, and Lumière and Seyewetz (*Bull. Soc. Chim.*, 1903, **29**, 1077) found that 100 grams of gelatin fixed 3·2–3·5 of Cr_2O_3 from any chromium salt solution. These observations appear to be in accord with Wilson's theory, though in the case of gelatin, Wood (*J. Soc. Chem. Ind.*, 1908, **25**, 384) could not confirm Lumière and Seyewetz's work, and stated that the amount fixed depended upon the concentration and basicity of the chrome liquor. He found in one instance that as much as 13·6 grams of chromium oxide had become fixed, which Wilson accounts for by postulating that conditions might prevail during a reaction which would favour the hydrolysis of gelatin

with the formation of more terminal amino and carboxyl groups, and thereby enable the gelatin to combine as a polybasic acid instead of as a monobasic acid. Hence the amount of Cr_2O_3 would be some multiple of 3.3, as was roughly the case in Wood's experiment.

The results of Thomas and Kelly (*Ind. Eng. Chem.*, 1922, **14**, 621) seem to support this idea; thus the maximum amount of chromium oxide adsorbed in 48 hours by hide powder was 13·4 grams for each 100 grams of protein, whereas when adsorption was allowed to continue for $8\frac{1}{2}$ months, a maximum of 26·6 grams was reached. The former is nearly four times the amount calculated by Wilson for the simple collagenate, and consequently was regarded as *Tetrachrone leather*, whereas the latter is slightly less than eight times, which therefore was an *Octachrome leather*. On purely arithmetical grounds, Wilson's idea may be considered satisfactory, but it is not so when viewed from the chemical standpoint. It will be remembered that collagen and gelatin act as bases, *i.e.*, with their $=NH$ and $-NH_2$ groups, at pH's less than the isoelectric point, *circa* pH 4·7, and as acids, *i.e.*, with their $-COOH$ groups, at higher pH's. Now, ordinary chrome tanning liquors invariably have lower pH's than pH 4·7, and in order for tanning to be the result of the combination of chromium with collagen carboxyl groups, it will be necessary for the chrome collagen compound to be extremely insoluble, such that the chromium might be able to react with the infinitely small amount, if any, of ionised carboxyl groups. Cobb and Hunt (*J.A.L.C.A.*, 1926, **21**, 454) considered that if tanning could be carried out with liquors at the isoelectric pH and above, when the dissociation of the carboxyl groups becomes the predominating feature, increased chrome fixation should occur. They found no such increase, but observed that chrome adsorption tended to become a maximum at about pH 6. In order to prepare liquors having varying pH's, they added either sodium acetate or formate in small amounts to the liquors, and added acid or alkali as required. Cobb and Hunt favour the view that chrome tanning is merely the outcome of physical adsorption on account of the large surface provided by the hide substance. This presumably would depend largely upon the sign of the electric charge carried by the collagen and the chrome. At pH's below 4·7, collagen bears a positive charge, and consequently for the coagulation of a chrome sol at the surface of collagen, it would be expected that chromium hydroxide particles would be electronegative. Actually, they may be either electropositive or electronegative, and according to Stiasny and Lochmann (*Collegium*, 1925, 200) equally good

leathers can be produced with chrome liquors whose chromium hydroxide migrates to either the anode or cathode when under the influence of the current. Stiasny (*Z. angew. Chem.*, 1924, **37,** 913 ; *Gerber*, 1924, 183) attributes the loss in tanning action of chrome liquors to which addition agents, *e.g.*, sodium acetate, oxalate, and sulphite have been added, to the formation of chromium compounds in which all the so-called secondary or auxiliary valencies are saturated. Hence the ability of a chrome liquor to tan is connected with the presence of unsaturated secondary valencies, and consequently chrome tanning is the outcome of the direct attachment of collagen to a central chromium atom by means of residual valency forces whose magnitude and also the stability of the compound formed, are a function of the composition of the internal sphere. Such a theory is probably incapable of proof.

In addition to the chromium hydroxide fixed by the pelt, appreciable amounts of acid radical from the tanning liquors are also fixed, some of which is removed by subsequent neutralisation. In the opinion of the author, chrome tanning is the result of (*a*) combination of collagen with some acid radical, (*b*) precipitation of basic chromium salt on the fibres, and (*c*) the rendering of the basic chrome salt less readily soluble by " ageing." Neutralisation of the tanned leather is apt to remove the acid in combination with the collagen and to a certain extent from the deposited basic chrome precipitate.

The curve in Fig. 167 referring to the reaction of sodium hydroxide upon a basic solution, having the composition $Cr(OH)SO_4$, prepared by reducing potassium dichromate with sulphur dioxide and boiling until the excess of sulphur dioxide was expelled, gives an idea of the type of reaction which a basic chrome liquor undergoes after penetrating into the hide. The interaction of the hydrolysed acid with the collagen causes a rapid increase in *p*H, and thus facilitates precipitation at the collagen interface in the form of a basic chromium salt. It is here that the proximity of the precipitation *p*H of chromium hydroxide to that of isoelectric collagen plays such an important *rôle*, for it is likely that the slight hydrolysis of the collagen hydrosulphate will not affect the *p*H to any great extent, as the hydrolysis will be suppressed through being confined within the pelt. Similar remarks apply also to alum and iron tanning. As far as the author could ascertain electrometrically, the presence of gelatin in an aluminium or chromium salt solution, whilst these are undergoing precipitation with sodium hydroxide does not affect the hydrogen-ion concentrations, as would probably have occurred if gelatinates

had been formed. Sheppard, Sweet, and Benedict (*J. Amer. Chem. Soc.*, 1922, **44**, 1857), from hydrogen electrode titrations of gelatin solutions to which varying amounts of alum were added, concluded that the effect of the latter was to displace the iso-electric point of gelatin to about *p*H 4·2. This *p*H, however, is the precipitation *p*H of aluminium hydroxide (*vide* p. 70). Their measurements of the rigidity of gelatin containing alum at different *p*H's are significant in that they show that alum produces a tougher gelatin. Sheppard (*Ind. Eng. Chem.*, 1922, **14**, 1025) has recorded the effects which varying amounts of alum may have on the melting-point of gelatin. The highest melting-points were obtained when the *p*H happened to be that required for the precipitation of aluminium hydroxide, and they fell rapidly for *p*H's on either side. When precipitation was prevented within the gelatin by means of citric acid the maximum melting-point occurred at the same *p*H, but to a considerably reduced extent.

It is probable that these conditions also refer to chrome leather as far as its resistance to heat is concerned (*cf.* Schiarparelli, *J.S.L.T.C.*, 1925, **6**, 413). It may be that the cause of this change at, and above, the precipitation *p*H is due to the gelatin fibres, or particles, becoming encased with basic aluminium sulphate, which actually is first precipitated, and not the pure hydroxide, and that this casing becomes impaired as the *p*H is raised through the progressive decomposition of the basic precipitate. It would appear, therefore, that in the neutralisation of leather, great care should be taken to neutralise only to the respective precipitation *p*H, for chrome *p*H 5·3, and for alumina *p*H 4·1 (see, however, Mudd and Pebody, *J.S.L.T.C.*, 1929, **13**, 205; Schindler, Klanfer and Flaschner, *Collegium*, 1929, 472).

CHAPTER XXXVI

THE IMPORTANCE OF HYDROGEN-ION CONCENTRATION IN THE VEGETABLE TANNING OF LEATHER

The nature of the constitution of vegetable tanning materials still remains obscure, though much has recently been done which throws light upon the subject. Perhaps the most important advance was made by Emil Fischer in 1918 in synthesising gallo-tannic acid, the tannin of oak galls. Pure organic chemical research will undoubtedly assist in the development of leather chemistry, but the results forthcoming from physico-chemical investigation are certainly of greater immediate value.

Tannins precipitate gelatin from solution, very probably through the coagulation of oppositely charged colloids and to some extent the formation of an insoluble and indefinite gelatin tannate, which is not decomposed by water. A similar reaction, no doubt, occurs with collagen. The actual tannins in tanning liquors are colloidal, but it is hardly permissible to state that the tanned insoluble bodies are merely colloids because they are the outcome of the coagulation of two simple colloids. Chemical forces come into play, for the tannins are weakly acidic in their behaviour, and in acid solutions of hydrogen-ion concentration greater than about pH 5 collagen behaves as a base. Tanning extracts contain non-tannins which are crystalloidal and are therefore diffusible and do not combine with the proteins. Nevertheless, as Wilson and Kerr (*Ind. Eng. Chem.*, 1920, **12,** 1149) found with completely detannised liquors, the non-tannins may produce tannins on oxidation. Perhaps the view of Wilson and Kerr (*ibid.*, 1920, **12,** 465 ; 1921, **13,** 772), that tannin is that organic matter which combines irreversibly with hide substance, offers the best practical definition.

Thomas and Foster (*ibid.*, 1922, **14,** 191 ; 1923, **15,** 707) have shown by electrophoresis experiments that the different vegetable tanning materials at their natural reaction, about pH 4, migrate anodically ; in other words, they are negatively charged colloids and therefore behave as acids. On increasing the hydrogen-ion concentration the migration speeds become reduced, until at pH values between 2·5 and 2·0, the direction of the movement undergoes a reversal. Many of the commonly used tannins there-

after suffer precipitation. The reversal is probably due to the growth of the particles to the state of hydrophobic suspensions and then they adsorb hydrogen ions, as is the case with charcoal.

A variation in the pH of vegetable tanning liquors may have a pronounced effect on their colours, and consequently on the resulting leathers. Thus Wilson and Kerr (*Ind. Eng. Chem.*, 1921, **13**, 1025), who studied the effects produced on gambier and quebracho liquors when left exposed to the air for differing lengths of time at different pH values, found that the colour changed from a light straw at pH 3 to a very deep red at pH 12. This colour-change is reversible if the liquors are acidified before they have long been exposed to air, but after a little time the liquors become darker in the more alkaline solutions and do not regain their original bright colour on bringing to pH 3. This indicator-effect accounts for the dark colour of a tanned skin from which the lime had not been completely removed, though such a colour may often be brightened if the leather is treated with acid soon after tanning.

In some experiments carried out by R. O. and A. W. Page (*Ind. Eng. Chem.*, 1929, **21**, 584) on tanning of bated ox-hide by means of liquors prepared from wattle bark and chestnut wood extracts and adjusted to pH values ranging from 1·0 to 9·0, they found that the tan liquors showed a variation with pH. The colour was palest at pH 5, darkest at pH 2 but brightened towards pH 1 though it developed an increased reddish tint, darkened gradually from pH 5 to 7 and more so at pH 8–9, especially with the chestnut liquors. Pre-treatment of the hide with buffer solutions of high or low pH caused a darkening in the colour assumed by the tanned leather. Subjection of the hide first to buffer solutions at pH 5, then tannage in wattle-bark liquors at pH 5 and finally in liquors ranging in pH from 1 to 9, gave to the tanned leather colours which were lightest from pH 1 liquor and darkest from the pH 9 liquor, regular variations being produced by the liquors of intermediate pH.

Another observation of Wilson and Kerr on the consequences of leaving certain vegetable tanning solutions having high pH values exposed to the air, is of interest, namely, that after keeping a liquor at pH 9 for 24 hours it produced a voluminous precipitate on acidifying back to pH 3. In solutions of lower pH values this effect was considerably reduced as regards speed, and curiously enough it did not take place at all in solutions more alkaline than pH 9.

The adjustment of the pH of acid-dye baths has been found by Woodroffe and Hill (*J.S.L.T.C.*, 1930, **14**, 203) to be an

important factor in the dyeing of sumac-tanned leather. Maximum colour was obtained in most cases at pH 2.

The influence of hydrogen-ion concentration, the concentration of the tanning liquors, and the time allowed for tanning have been very carefully investigated by Thomas and Kelly (*Ind. Eng. Chem.*, 1923, 15, 1148), using hide powder and six different tannin extracts, *viz.*, quebracho, gambier, hemlock bark, oak bark, larch bark, and wattle bark. To ascertain the amount of tannin fixed, they adopted a method introduced by Wilson and Kerr (*loc. cit.*), based on the definition of tannin given above. The determinations simply involved the measurement in the increase in weight of a sample of hide powder, after tanning and thorough washing in order to remove the non-tannins. The curve marked
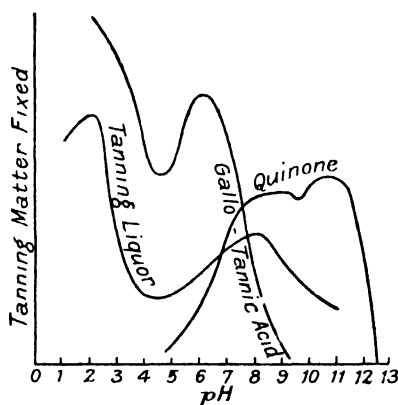
FIG. 168.—Variation with pH of Tannin fixed by Hide Powder.

" tanning liquor " (Fig. 168) expresses the general nature of their results, though, of course, the shape was affected by the particular tannin extract used, its concentration and the time of tanning. Thus with a prolonged time of tanning, there was a tendency for the minimum at pH 5 to disappear. It will be observed that the curve is similar to the swelling curves of collagen and gelatin. The minimum fixation will be seen to have occurred at pH 5, which is approximately the isoelectric point of collagen. The curve shows that an increase in the fixation of tannin occurred from pH 5 to pH 2 ; a fact which is in harmony with the acid nature of the true tanning agent. It is difficult, however, to visualise why tannin should have been fixed on the alkaline side of the isoelectric point. Wilson and Gallun (*Ind. Eng. Chem.*, 1923, 15, 71) found, in investigating the plumping of calf skin at 7° C. in regard to the concentration of hydrogen ions, that

there were two minimum points of plumping, at pH 5·1 and pH 7·6. To explain this they suggested that these two minima represent the isoelectric points of two different forms of collagen. If therefore, it be assumed that the pH range 5·1 to 7·6 corresponds to some internal rearrangement from the ordinary form, the iso-electric point of which is at pH 5, to another having pH 7·6 as its isoelectric point, then tannin fixation above pH 5·0 must be attributed to combination with the second form. (See, however, Fig. 164.) This explanation should be taken with reserve.

Vegetable tanning extracts contain organic matter of the nature of quinone, and moreover, certain non-tannins which, on oxidation by the air, give quinone-like substances in alkaline solutions. Such bodies have tanning action. Thomas and Kelly (*Ind. Eng. Chem.*, 1924, **16**, 925) have studied the rate of tanning with benzo-quinone at different pH values. The curve marked " quinone " in Fig. 168 illustrates their results and shows that the tanning action of quinone comes into play above pH 6.

It might be concluded that the presence of quinone derivatives in the tannin extracts would supply an adequate explanation of the tanning at pH values higher than 5, but in another paper by the same workers (*Ind. Eng. Chem.*, 1924, **16**, 800) it has been demonstrated that tannic acid, which was rendered free from quinone-like substances, and also reasonably free from non-tannins, still was able to produce an increased tannin fixation in the region of pH 7. The curve labelled " gallo-tannic acid " depicts their results, from which it appears that tannic acid fixation as such is not possible above pH 9. The tanning action of vegetable tannins between pH 8 and 12 is considered to be due to substances of the nature of quinones (*ibid.*, 1926, **18**, 625).

Gordon and Gilman (*J.I.S.L.T.C.*, 1927, **11**, 213) have directed their attention to the importance of hydrogen-ion concentration in vegetable tanning, and in order to obtain results which reproduce practical tannery conditions more satisfactorily they used partially delimed ox-hides and a tanning liquor composed of a blend of Valonia, Myrabolams, Mimosa bark, and chestnut extract, which is similar to that commonly used in English tanyards. They estimated the total amounts of tanning matter which had been adsorbed after the hides had undergone different periods of tanning. Their results are given in Fig. 169, in which the numbers correspond to the number of days of tanning. These curves do not represent the true degrees of tannage, for considerable proportions of non-tannins are included. The broken curve gives the true degree of tannage after 42 days, whereas the top curve gives the apparent tannage in the same time.

The curves show an increased tannin fixation when the liquors were about pH 2. Gordon and Gilman, however, found the resulting leather to be of little commercial value as it was harsh and brittle and had an unsatisfactory colour. When tanned at pH 2·5 the leather was found to be firm and was not brittle, though its colour was not all to be desired. Their results show that tanning at pH 3 gave rise to a leather which appeared to have the properties most desired in sole leather, *viz.*, firmness without brittleness, good substance and colour and a fairly high percentage of tannin. The increase in pH had one disadvantage in that it tended to promote " bloom " deposition and this appeared on the leather in question. The samples tanned at pH 4·0 and 5·0 had heavy deposits of " bloom," though both leathers were mellow and of good colour.

Fig. 169.—Variation with pH of Vegetable Tanning Matter (Tannin and Non-Tannin), absorbed by 100 parts of Partially Delimed Ox-hide.

As regards the suggestion of Thomas (*J.A.L.C.A.*, 1926, 21, 513) that the best results would probably be obtained by tanning at a pH in the neighbourhood of the isoelectric point of collagen, *i.e.*, 4·5 to 5·0, so as to secure better penetration of the tanning liquors and then to increase the tannin fixation and the plumping of the hide by lowering the pH of the tanning liquor to pH 3, Gordon and Gilman point out that it is a matter for further investigation as to whether any very marked plumping would occur once the pelt is struck through.

                                                    40, 136) observed that the minimum fixation of quebracho by leather occurs at pH 5·0 and pH 7·5, these pH values corresponding to the minimum swelling of the pelt. Between pH 5 and pH 8 the fixation of vegetable tannin is analogous to that of benzoquinone, which is rapidly fixed by collagen at pH 7·0 and slowly at pH 5·1.

Some of J. A. Wilson's data (*Cuir Tech.*, 1936, 100), showing the comparative tanning capacities of tanning extracts towards

TABLE 206[f]

Extract.	% Combined Tan in Leather.	Final pH of Leather.	Time required for Penetration (Days).
Gambier	69·61	4·37	16
Chestnut	64·55	3·20	14
Oakbark	44·04	4·55	30
Sulphited Quebracho . .	40·47	6·07	10
Valonia	37·61	3·83	20
Mimosa	37·15	4·76	11
Quebracho	29·63	5·21	18
Myrobalans	27·45	3·13	33

leather which was immersed in liquors of gradually increasing concentrations for 42 days, are recorded in Table 206.

The part played by hydrogen-ion concentrations in vegetable tanning has also been investigated by Pavlovitsch (*Collegium*, 1928, 2), and Stather and Schubert (*Collegium*, 1934, 609). Contrary to the observations of Thomas and Kelly, Fig. 168, Pavlovitsch found that there is a minimum tannin fixation at pH 6–8, although it often happens that in more acid solutions the rate of penetration assumes a maximum value, *e.g.*, at pH 4 using chestnut. In consequence, Pavlovitsch (B.P. 302,408/1927) suggests the use of strong liquors at pH 6–8 until the hides are coloured through and then bringing the pH gradually to 3–4 in order to fix the tannin already within the hide. The latter workers find that the thickness of leathers tanned with extracts of chestnut-wood, oak-wood, sumach, mimosa bark, myrobalans, valonia and sulphited quebracho decreases with rise in the pH of the tanning solution. Natural quebracho, mimosa, gambier and oak-bark extracts give leathers which are unaffected by the pH of the solution. Increase in pH raises the tensile strength of most leathers, but, with the exception of mimosa and natural quebracho, it yields less stretchy leathers. According to Thomas and Kelly (*J.A.L.C.A.*, 1929, **24**, 282) the fixation of tannin between pH 2·5–3·0 is influenced by the nature of the acid, weak acids having the greater effects.

For the manufacture of sole leather, Rezabek (*J.S.L.T.C.*, 1936, **20**, 72, 209) advocates varying the pH of the tanning bath from 8·0 to 3·0 towards the end of the process. Maximum tannage is obtained at low pH. By operating over a pH range, from 8 to 3, intermediate swelling was given to the fibres.

The rate of penetration of the tanning agents into the pelt is greatly retarded when the pH falls below 3·5 (Wilson, *J.A.L.C.A.*, 1936, **31**, 449 ; Rezabek, *J.S.L.T.C.*, 1936, **20**, 530). Combina-

TABLE 207 •

Tannage.	c.c. 0·1.N.HCl fixed by 1 gram of Collagen.	pH.
None	0·94	—
Quebracho	0·88	5·5
Mimosa	0·88	4·8
Myrabolam	0·78	3·2
Lignosulphonic acid . .	0·04	1·3

Red. From the difference between the original and the final titres of amounts of hydrochloric acid that combined with 1 gram of collagen were found. Very little hydrochloric acid was taken up by the collagen that had been tanned with lignosulphonic acid, thus showing that the tanning action of lignosulphonic acid is fundamentally different from that of the vegetable tannins (see also Baum, Lovin and Salvesen, *J.A.L.C.A.*, 1952, **47**, 269).

The presence of ferric tannate in tan liquors above pH 2·7 leads to the staining of leather. The tannate can be precipitated as ferric phosphate at pH 5·2 (Balfe and Phillips, *J.S.L.T.C.*, 1934, **18**, 592).

Mineral and oxalic acids give rise to the acid rotting of leather. Colin-Russ (*ibid.*, 1937, **21**, 628) measures the pH of the water filling the interstices between, and adhering to, the fibres when the leather is saturated with water. The pH should not be lower than pH 2·8–3·0. The use of sulphonated cod oil is a source of such acidity. Bowker, Wallace and Kanagy (*J.A.L.C.A.*, 1934, **29**, 623 ; 1935, **30**, 26, 91, 438) state that the sulphuric acid liberated therefrom lessens the tensile strength of leather tanned with quebracho-wood extract. Oxalic acid leather, pH of about 3, leads to the deterioration of quebracho and chestnut tanned leather in two years.

Determination of pH values of Tanning Liquors.

Difficulty is often encountered in measuring electrometrically the pH of tan-liquor on account of the disturbing influences that may often be present. For this reason, care should always be taken to ascertain that reproducible results are being obtained when using either the hydrogen or quinhydrone electrodes. Both have been found to lead to erroneous results (Wallace and Beek, *Bur. Stand. J. Res.*, 1930, **4**, 737 ; Goldman, *J.S.L.T.C.*, 1930, **14**, 211 ; Hepburn, *ibid.*, 1930, **14**, 261). According to Pleass (*J. Soc. Chem. Ind.*, 1929, **48**, 152T) the quinhydrone electrode is untrustworthy in all trade tan liquors. She has

demonstrated, however, that the glass electrode is reliable in all kinds of liquors.

The colorimetric determination of the pH values of coloured solutions is often a matter of some difficulty. It is stated that measurements, accurate to 0·1–0·2 pH, may be made in 2 minutes by means of the Wulff " Folien Colorimeter " (*Leather Tr. Review*, 1929, **62**, 506), in which small celluloid strips are impregnated with suitable indicators.

Thompson and Atkin (*J.S.L.T.C.*, 1929, **13**, 111) have designed a method by which the pH of dark-coloured solutions may be evaluated from the colorimetric readings of diluted solutions whose colours have thereby become sufficiently pale. They dilute 2, 4, 8, 16 and 32 times and, if possible, determine the pH values of the diluted solutions. The pH values are plotted against the logarithm of the dilution of the *water already in the leather* by the added water and from the curve so obtained the pH of the original solution is extrapolated. These authors have also evolved a method of ascertaining the pH value of vegetable-tanned leather. This method involves the assumption that the water-content of leather is 14 per cent. and the pH values of liquors obtained by extracting varying amounts of the leather with potassium chloride solution (*J.S.L.T.C.*, 1929, **13**, 300). Thus 2 grams of leather contain 14 per cent. of water, *i.e.*, 0·28 c.c. of water. On adding 100 c.c. of water (actually 0·1 M.-KCl solution) the total water becomes 100·28 c.c., when the dilution is 100·28/0·28 = 358.

The presence of free sulphuric acid in vegetable tanned leather causes deterioration, and its detection therefore becomes a problem of some importance. Innes (*J.I.S.L.T.C.*, 1928, **12**, 256) made use of the fact that the ten-fold dilution of a solution of a strong acid increases the pH by *one* whole pH unit, whereas dilution of a weak acid causes a considerably smaller increase. For example, acetic acid gives an increase of about 0·5 pH unit. If, therefore, the difference between the pH of the leather extract and of the extract, diluted 10 times, is less than 0·6, the leather is considered to be free from mineral or harmful acid. Should the difference be 0·7 or greater, the criterion of harmful acid is the initial pH. Leathers giving pH 3 or higher are regarded as free from mineral acid, whilst an initial pH lower than 3 indicates the presence of harmful quantities of mineral acid. Otto (*Collegium*, 1933, 586) deduces the existence of harmful free acids from the steepness of the electrometric titration curve (with NaOH) between pH 3·5 and 4·0.

Innes (*J.I.S.L.T.C.*, 1934, **18**, 457) has applied an observation

of Richardson (*Proc. Roy. Soc.*, 1934, B, **115**, 170) that in a
90 per cent. acetone-water solution the ionisation of weak acids
is almost entirely suppressed, whilst that of strong mineral acids
is not, and they can therefore be titrated to pH 3·4. Innes
extracts 10 grams of leather with 100 c.c. of water, and then
dilutes 5 c.c. of the extract with 45 c.c. of acetone. If the pH is
3·4, it corresponds to 0·2 per cent. H_2SO_4 in the leather, whereas
between pH 3·4 and 4·0 less than 0·1 per cent. of free H_2SO_4 is
indicated and above pH 4·0 no mineral acid is present.

To obviate errors due to the titration of carbonic acid and
phenolic groups, Burton (*J.S.L.T.C.*, 1948, **32**, 362 ; Atkin and
Burton, *ibid.*, 1949, **33**, 52, 271) titrates the strong and weak
acids in vegetable tanning liquors to pH 5·8. The weak acids
are estimated by back-titration to pH 2·0 or 2·8. By titrating
to pH 2·0 data were obtained which are similar to those obtained
by Balfe (*ibid.*, 1948, **32**, 39) using a base-exchange resin method.

CHAPTER XXXVII

THE IMPORTANCE OF HYDROGEN-ION CONCENTRATION IN SUGAR MANUFACTURE

THE regulation of the acidity or alkalinity of the various sugar solutions during the purification processes involved in the manufacture of sugar has always been a problem of paramount importance. Until quite recently, it was customary to investigate it only in terms of the titres obtained, when the juices were titrated with either alkalis or acids in presence of the commoner indicators. Though such a method undoubtedly provided data of value for the purpose of control, especially when the juice or beet employed in the particular refinery was obtained from one special source and the initial solutions were of an approximately constant concentration of the non-sugars, the data, however, became of little technical use when raw materials obtained from different sources were compared, and led to unsatisfactory results when attempts were made to use them to standardise the processes adopted in different manufactories. The variable acid contents, inorganic and organic, in sugar juices gave rise to different titratable acidities, which very often, due to the varying buffering effects of the several acids, were not in any way comparable with the hydrogen-ion concentrations of the solutions, on which it is now known that the efficiency of refining is very largely dependent.

Before dealing with the part played directly by hydrogen ions, it will be necessary to consider for a moment some of the principles underlying sugar manufacture. Sugar refining is essentially a process of fractional crystallisation from liquors which are more or less impure. It is well known that crystallisation may be very considerably influenced by the presence in the mother-liquor of substances which are colloidal in nature. The dispersed particles generally have an impeding effect upon crystallisation, and when once this has taken place the colloidal particles often contaminate the crystals in such a way that the impurities are not easily removed. The important problem then is the efficient purification of the liquors from which sugar crystals are eventually to be obtained. Hence the need of knowing at the outset the composition of the solutions and juices.

The juice squeezed out of sugar canes by milling comprises

the sugar sap, the soil water and protoplasm, the proportions of which depend upon the pressure exerted between the rollers. The sucrose content of the canes varies from 11 to 16 per cent. About the same amount of fibre, or *bagasse*, remains after milling. According to Heriot (" The Manufacture of Sugar from Cane and Beet," London, 1920), a typical analysis of an undiluted cane juice is : Water, 83·0 per cent. ; sucrose, 15·0 per cent. ; reducing sugars, 1·0 per cent. ; organic non-sugars, 0·5 per cent. ; mineral matters, 0·5 per cent. Such a juice is 17.0° " Brix," *i.e.*, the sum of the percentage amounts of solutes, and the " purity " of the sugar is $15/17 \times 100 = 88·2$ per cent. The pH of sugar-cane juices varies somewhat from locality to locality, but the juices from any particular locality do not exhibit any great variation. Thus for the whole of the Louisiana sugar producing area the range is pH 5·2–5·6. Fort and Lauritzen (*Ind. Eng. Chem., Anal. Edn.*, 1938, **10**, 251) point out that for such juices a pH below 5·20 indicates souring, which may have resulted from freezing. With this fall in pH, there is a corresponding rise in titratable acidity. The reducing sugars are glucose and fructose. The organic non-sugars include such acids as glycollic, malic, oxalic, succinic, tannic, and from diseased canes, acetic. They also include certain nitrogen compounds, some of which are distinctly colloidal, *e.g.*, albumin, albuminoses, amines and amino-acids, nucleins, peptones, etc. ; colouring matters, *viz.*, anthocyanin, saccharetin and chlorophyll ; and such substances as pectin and gum (xylan). The mineral matters which account for the ash are derived from the soil and contain phosphates, chlorides, sulphates, nitrates and silicates of aluminium, iron, calcium, magnesium, sodium, and potassium. Anthocyanin is the dark colouring matter in the rind of purple canes. It is both difficult to remove completely and to bleach with sulphur dioxide in the course of sugar manufacture. Saccharetin, though colourless in acid solutions, becomes bright yellow in alkaline solutions, and is regarded as the cause of the colouring of the so-called " Demerara sugar." Though it cannot be precipitated with acids or alkalis, it can be bleached with sulphur dioxide. That tannins and polyphenols are sometimes found in sugars may be concluded from the greyish tinge which they assume, and especially is this the case when iron vessels have been used. To prevent inversion of the cane sugar from taking place when the juice is concentrated by boiling, it must not contain any acid, and milk of lime is therefore added until the juice has just become alkaline. This causes some non-sugars to be precipitated. Calcium oxalate is also thrown out of solution as " scales " and so, too, is a little

of the phosphoric acid as the calcium salt.   Care here is necessary to avoid too great an alkalinity, or it will cause the decomposition of reducing sugars with the production of the calcium salts of lactic, glucinic and saccharinic acids.   Calcium salts of acetic, glycollic, succinic and malic acids should be avoided in the juices, for if they are allowed to pass into the molasses adhering to the raw sugar crystals, they, being hygroscopic, will cause the crystals to become moist and so reduce their commercial value.   On the other hand, certain bacteria flourish in cold alkaline juices which convert the sugar into the gummy substances, dextran and levan, and lactic and acetic acids.   Acidity, such as may be produced by the latter, will in time kill these organisms.

As the composition of the original sugar solution, obtained from sugar canes, is determined to some extent by the manner in which the milling is effected, so, too, in the beet industry, the initial solution depends upon the process of diffusion into water of the juices contained in special types of beets, after they have been cut into slices.   If no cells were cut open in the act of slicing, then the diffusates would be crystalloids, the colloids, such as the proteins, being unable to pass through the cell-walls. Actually, some proteins contained in the fractured cells do pass into the diffusion juice, which proteins become coagulable on heating.   The sucrose content of sugar beets ranges from 12·7 to about 18 per cent., and the amounts of reducing sugars are considerably lower than in cane juice.   The diffusion juice is often opaque, grey, or yellowish in colour, darkens readily in air, and has a specific gravity of from 1·048 to 1·063 (*i.e.*, 12° to 15° Brix.). It contains from 10 to 14 per cent. of sucrose, 0·4 to 1·7 per cent. of organic non-sugars, and 0·3 to 0·6 per cent. of mineral matters. The organic acids in beet juice differ somewhat from those in cane juice, the following having been found to be present : aconitic, citric, glycollic, malic, oxalic, succinic, and tartaric.   Phosphates, sulphates, nitrates, and silicates are also present.   Besides the usual protein derivatives, catechol, which in conjunction with iron salts provide some of the colouring agents. Cholesterol, glucosides, pectins, pentosans, lecithin are often to be found.   Condensation products of amino-acids and reducing sugars give rise to some of the colouring.   The mineral matters are similar to those in cane juice.   Much of the colour of sugar juices, which escape bleaching with sulphur dioxide, can be removed by treatment with bone-chars, which act as adsorption agents.

In order that sugar may diffuse from the cells of the beet, the protoplasm in the cells must be destroyed.   In the usual diffusion process this is effected by the high temperature em-

ployed, which, however, causes the pectins and other non-sugars to dissolve. Malinovski (*Zentr. Zuckerind.*, 1932, **40**, 442) destroys the protoplasm by steeping the beet cossettes in an equal weight of 0·07 N-H₂SO₄, which gives a clear yellow juice and one which is easier to manipulate. A similar method has been described by Spengler, Tödd and Böttger (*Z. Ver. d. Zucker-Ind.*, 1932, **82**, 650), who also use sulphuric acid at 15° and subsequently adjusts the *p*H near to that of the isoelectric point of the protein colloids in order to bring about their coagulation in the cossettes and so prevent their diffusion. Vasatko (*Z. Zuckerind. Czechoslov.*, 1934, **59**, 65, 149) and Schonebaum and Moen (*Intern. Sugar J.*, 1935, **37**, 303) coagulate the colloidal material from beet sugar juice by bringing the *p*H to 4.

Not only are the sugar crystals affected by the adhesive coatings of molasses, but the " grain " of the crystals themselves is to some extent determined by the insoluble matter in the juices ; the incorporation of insoluble material in the crystals tending to make them small and unsatisfactory. A considerable proportion of the molasses which contaminates the raw sugars obtained from the initial concentration can, if the sugar crystals are of satisfactory grain, be removed by the process known as " affination." Thus, raw sugars, separated by means of centrifugal filtration, may be as much as 96 per cent. pure when obtained from mother-liquors or molasses, whose purity vary from 65 to 75 per cent. Such crystals and molasses may be obtained from raw juices, which before boiling were from 80 to 88 per cent. purity. It is legitimate to assume that crystals so prepared having 96 per cent. purity would be composed of almost pure sugar, say, 99 per cent. purity, and a little molasses constituting a skin of about 70 per cent. purity. It so happens that the molasses or syrups of low sugar contents, but with comparatively high contents of non-sugars, *i.e.*, syrups of low purity, can be obtained, which constitute solutions saturated with respect to sucrose but which are unsaturated with respect to non-sugars. Hence, these solutions, though unable to dissolve more sucrose, will still be able to dissolve non-sugars, a property which is taken advantage of in the process of affination. The raw sugar crystals are therefore subjected to treatment in suitable mixers, " minglers," with suitable low-purity syrups which extract much of the impurities. Incidentally these syrups become high in non-sugar content, and in order to use them for the production of sugar crystals they must undergo rigorous and carefully controlled chemical treatment so as to precipitate as much of the non-sugars before further crystallisation of sugar is attempted.

The remaining part of this chapter will be devoted to the

chemical methods which **a**re employed for the purification of sugar solutions.   It was stated earlier that a little calcium phosphate was precipitated when the acidity of the milled cane juices was adjusted by the cautious addition**s**of lime cream.   The amount of phosphoric acid thus removed, however, is negligible when compared with that which is left in solution, and consequently that part of the process cannot be considered to have any refining value.   Sugar juices, to which the non-sugars have been translocated by means of the affinating process, undergo one or more of the following treatments : *defecation, sulphitation,* and *carbonation.* For the manufacture of raw cane sugar either " defecation " or " neutral-sulphitation " is employed, whereas for white cane sugar both acid-sulphitation and carbonation are often adopted. The chemical treatment given to beet is usually carbonation which is very often carried out in two stages, though this procedure is sometimes combined with one of sulphitation.   It should be mentioned here that when sulphitation is applied prior to carbonation, the calcium precipitate is so gelatinous that it becomes very difficult to manipulate.

The rate at which colloidal substances undergo coagulation from beet-sugar liquors acquires a maximum value at *p*H 3·2 (E. Gundermann, *Chem.-Ztg.,* 1929, **53,** 305), and the proportion of sediment is also then at a maximum.   Coagulation at *p*H 3·2 results in a better appearance of the liquor, whilst addition of acid leads to a darker colour.

Defecation.

Defecation is a process by which the sugar juices are clarified by the addition of slaked lime in such quantities as to cause the maximum precipitation of calcium phosphates in the flocculent condition.   There are limits to which liming can be safely conducted, for if too high *p*H's are attained the " invert " or " reducing " sugars will undergo decomposition on boiling.   King and Torres (*Sugar News,* 1934, **15,** 78) emphasise that the use of much lime decomposes the invert sugar into acid products.   The physical condition of the phosphate precipitate causes it to adsorb part of the colloidal impurities, but the amount actually carried down depends upon the amount and nature of the precipitate produced.   Ordinarily, this is determined by the quantity of phosphoric acid in the juice, and in cases where it is found to be insufficient, phosphoric acid is sometimes added.

Britton (see p. 144) has investigated the precipitation of phosphoric acid with calcium hydroxide from aqueous solutions, and also from acid solutions containing sucrose.   When precipi-

tation was carried out at 20° C., it was found that a precipitate did not begin to appear until pH 6·7 had been attained and 1·5 equivalents of lime water had been added. The variation in hydrogen-ion concentration was similar to that shown in Fig. 170, which gives the pH neutralisation curves of phosphoric, sulphurous, and carbonic acids. The greater parts of these curves will be unaffected by the concentration of acid taken except the first halves of the sulphurous and phosphoric acid curves and the last portion of the carbonic acid curve. They have been drawn for M/100-acid solutions. By comparing the curve given in (Fig. 58, Vol. I) for calcium hydroxide with that using sodium hydroxide, it will be seen that much of the delay in precipitation

EQUIVALENTS NaOH
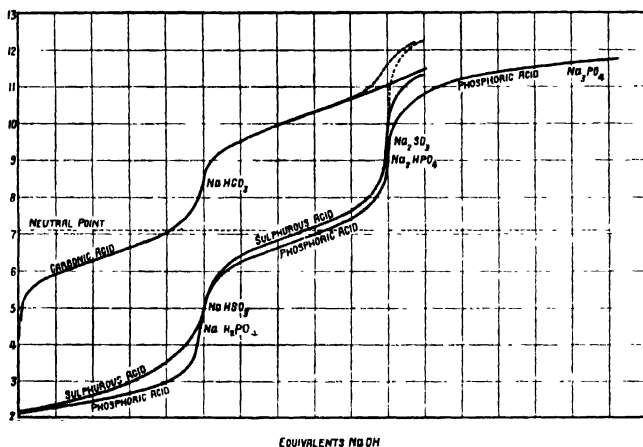
FIG. 170.—Titration Curves of Carbonic, Sulphurous and Phosphoric Acids.

was due to the tendency for the normal neutralisation pH change on adding lime to be followed, thus saturating the solution with respect to calcium phosphate. It was calculated, however, if time were allowed for the attainment of equilibrium that calcium phosphate would begin to separate at pH 5·5. Sucrose had very little effect on the precipitation of calcium phosphate as far as hydrogen-ion concentration was concerned. Farnell (*J. Soc. Chem. Ind.*, 1926, **45**, 343T) studied this problem more particularly from the point of view of the sugar refiner and found that, when boiling was carried out, a pH of about this order was necessary. An examination of the muds obtained from juices which had been limed to phenolphthalein, pH 8·4, by Paine and Balch (*The Planter and Sugar Manufacturer*, 1927, **78**, 127, 148) revealed that 20 per cent. of total mud was mineral matter.

According to Bond (*Intern. Sugar J.*, 1925, 311) such an ash contains principally the phosphates of calcium, iron, aluminium, and magnesium. Iron and aluminium are exceedingly difficult to remove as hydroxides, owing to the protective effect which sugar has upon them in retaining them in a comparatively stable colloidal solution. Cane juices also contain 400–700 mg. per litre of silica. Low *p*H values facilitate its removal (Honig, *Archief*, 1934, 435, 561.) About one-third of the silica is precipitated at *p*H 8. If the sugar juice does not contain sufficient phosphoric acid to enable the iron to be precipitated, the iron will have a deleterious effect upon the colour of the juice should any polyphenols be present. The organic non-sugars which are eliminated by liming from the juice constitute about 80 per cent. of total nitrogen compounds, *e.g.*, albumin, and very small percentage amounts of anthocyanin and pectin, but no cane gum. The amount of non-sugars removed from the juice depends to some extent upon the bulkiness and nature of the calcium phosphate precipitate, but, on the average, the amount so obtained is only about 11 per cent. of the total present. The juice, however, becomes transparent and yellow, and its purity increases by about one unit. The amount of calcium phosphate obtainable is also dependent upon the *p*H value to which liming has been carried out. The maximum *p*H for defecation is restricted to *p*H 8·25, for at this stage Bomonti (*Report Assoc. Hawaiian Sugar Technologists*, October, 1926) has found that the destruction of reducing sugars first becomes evident. A method which is claimed to improve the filtering properties of the defecation mud has been patented by the Borden and Oliver Continuous Filter Co. (U.S.P. 1,653,491). The mud is heated to 80°, treated with lime to *p*H 8·5, and then either phosphoric acid or superphosphate is added until the *p*H is 6·0–6·9.

Davies, Duncan and Yearwood (*Intern. Sugar J.*, 1936, **38**, 298), however, find that refractory juices may be clarified by liming to *p*H 6·4, heating to 99°–100°, cooling to about 82°, liming again to *p*H 7·6 and finally heating to 99°–100° C. Less lime is thereby required, the pentosans and colloids are more easily eliminated and the mud is less voluminous and more readily filtered. The manner in which the lime is added is a question of some importance and King (*Ind. Eng. Chem.*, 1931, **23**, 954) prefers continuous liming, with the " Zitkowski " automatic apparatus, to batch liming. As a rule, liming beyond *p*H 8 is inadvisable, owing to (i) the risk of destruction of invert sugar, (ii) redissolution of mineral substances, (iii) injurious effects of soluble calcium salts. Liming below *p*H 7 is suitable only for

juices of low phosphate content. The titratable acidity of limed juice increases and the pH falls by 0·3–1·1 of a pH unit. Iron and aluminium are almost completely removed at pH 8, but not more than one-half of these metals is precipitated at pH 7.

According to M. I. Nakhmanovich (*Nauch. Zapiski Sak. Prom.*, 1929, **7**, 265) filtration of beet sugar juices is best carried out at pH 7·0–7·5, for destruction of sugar begins below pH 7 and discoloration ensues by heating at pH 8.

From the chart, Fig. 171, which gives the various pH's at which precipitations encountered in sugar refining begin to take place and also the pH ranges within which inversion of cane sugar occurs and the invert sugars become converted into acids, it will be seen that the pH range available for defecation is from just below pH 7 to just above pH 8. (It should be mentioned here that the pH's at which tricalcium saccharate and certain non-sugars precipitate, given in Fig. 171, are approximate only.) Pardo (*Facts about Sugar*, 1930, **25**, 220) states that in Peru the best clarifications were obtained by liming to pH 8·0–8·2, but that the rate of settling could be increased by liming to pH 7·8 as determined by means of phenol-red. Bomonti, however, states that the maximum increase in purity of cane juice is generally secured when liming is carried up to pH 8·3 to 8·5, at which alkalinity the amount of decomposition of the reducing sugars is negligible. As Paine and Keane (*The Planter and Sugar Manufacturer*, 1927, **78**, 168) point out, not only the pH, but also the phosphoric acid content of the juice should be controlled. Smith (*Report Hawaiian Sugar Planters' Assoc.*, 1924) states that it seems impossible to obtain a clear limpid juice if the P_2O_5 content is below 0·02 per cent., and McAllep and Bomonti (*Hawaiian Planters' Record*, 1922, **26**, 122) conclude that if

FIG. 171.—pH Chart of Chemical Processes in Sugar Refining.

100 c.c. of juice contain more than 0·03 gram P_2O_5, clarification becomes easy, whilst if there is less than this amount the juice will be dim, the massecuites may boil slowly, and the raw sugar produced in the refinery may filter slowly. Farnell (*loc. cit.*) found that at least 0·005 to 0·01 gram P_2O_5 must be present in 100 c.c. in order that calcium phosphate may be precipitated to such an extent that it will adsorb a part of the colloidal impurities. He suggests that the addition of phosphoric acid to certain poor juices may consequently become economic. A great advantage of a high phosphoric acid content is that it will cause increased precipitation at a lower *p*H, which will promote good clarification by removing a greater proportion of colloidal matter and non-sugars and at the same time keep the *p*H well within the limits necessary to avoid the inversion and the destruction of reducing sugar. Moreover, the unprecipitated phosphoric acid will exert a suitable buffer action.

The clarification of beet diffusion juice is effected merely by treating with relatively small proportions of lime (usually less than 0·4 per cent. of the total weight of the beets). The amount is that required to bring the *p*H to 10·8–11 when the colloids coagulate. As the coagulum obtained on the large scale is generally unfilterable, the usual process is to add a portion of the requisite amount of lime at an elevated temperature and later to add the remainder. Spengler (*Z. Ver. d. Zucker-Ind.*, 1932, **82,** 1, 205, 479, 617, 653) adds a portion at 35°–40° C. for three minutes and then raises the temperature to 80° for the final liming.

It should be mentioned that the *p*H measurements are usually made on juice diluted to 15° Brix (15 per cent. solids), whereas the *p*H's with which the refiner is mainly concerned are those prevailing when the solutions become concentrated to 50° Brix (say) by heating. Walton, McCalip, and Hornberger (*Ind. Eng. Chem.*, 1925, p. 51) observed that whenever the quinhydrone electrode was used to determine the *p*H of samples of syrup higher than 40° Brix, the value found was always lower than that of the same sample when diluted to 15° Brix. A typical difference is a variation from *p*H 6·36 for a 46° Brix syrup to *p*H 6·61 after it had been diluted to 15° Brix. This should be borne in mind in the factory, or inversion may occur in the concentrated juice through commencing with too low a *p*H. Heating alone produces a diminution in the *p*H of limed juices, which may be due to the precipitation of calcium phosphate and the consequent buffer action of the phosphate left in solution.

Sulphitation.

The clarifying effect of sulphitation lies in the adsorption by calcium sulphite precipitates,of colloidal matter and soluble non-sugars. The process may be carried out in either of two ways : (a) lime cream may first be added to give a high pH, causing the juice to become very dark on heating, but giving a more complete precipitation of calcium pectate, anthocyanin, and gum, and then the lime is neutralised by passing in sulphur dioxide to a pH which will bring about the maximum precipitation of calcium sulphite without any decomposition of sugar ; or (b) to render the juice strongly acid by passing sulphur dioxide and then liming to a desired pH. As is well known, sulphurous acid does not bleach in alkaline solutions, and therefore the first method, viz., neutral-sulphitation, is only applicable for the manufacture of raw sugar, and the second method, "acid-sulphitation," for white sugar. The amount of sulphur dioxide added in method (b) varies from 0·6 to 2·5 grams per litre. After liming, the juice is heated to 100° C. and then run into tanks to enable the calcium sulphite and phosphate to settle. According to Bogtstra (Archief, 1934, II, **15**, 597) sulphitation is carried out in Java by one of the following processes : (i) sulphiting to pH 3·8–4·3, liming to pH 8·0 and final sulphitation to pH 7, or (ii) simultaneous sulphitation and liming below 70° at pH 9.

Spengler and Böttger (Z. Wirts. Zucker-Ind., 1935, **85**, 251) recommend a preliminary sulphitation (0·005–0·01 per cent. SO_2) of beet diffusion juice, and they claim that still better results are obtained by sulphiting the raw beet slices before diffusion with 0·003 per cent. SO_2. By so doing, the pH of the diffusion juice is 5·8, instead of the usual pH 6·2–6·4.

The pH change undergone when a solution of sulphur dioxide reacts with an alkali is given in Fig. 170. The curve refers to the titration of 100 c.c. of $M/100$-H_2SO_3 solution with $N/10$-NaOH. For the purpose, either the glass electrode or antimony electrode may be used (Britton and Robinson, Trans. Faraday Soc., 1932, **28**, 531). The buffered curve produced by the addition of the second equivalent of alkali is almost independent of the concentration of the acid. Slaked lime first reacts with a sulphurous acid solution to form a soluble salt, $Ca(HSO_3)_2$, over a pH range up to about pH 5. This range, incidentally, is that at which inversion can occur, and therefore the lime should be added as quickly as possible, and also in the cold. Farnell (J. Soc. Chem. Ind., 1925, **44**, 530T) has investigated the pH at which calcium sulphite begins to precipitate, and found that at 20° a precipitate

began to separate when **1·1** equivalents of calcium hydroxide had been added and a *p*H of 5·5 had been reached. Precipitation thereafter occurred progressively with increasing *p*H, 95 per cent. having separated at *p*H 7·4 and 100 per cent. at *p*H 9·2. When the solutions were mixed at 20° and then boiled, cooled and the *p*H determined, precipitation still occurred with 1·1 equivalents of calcium hydroxide, but at *p*H 5·2 ; 95 per cent. being precipitated at *p*H 7·0, and 100 per cent. at *p*H 8·8. Sugar had no retarding influence, but diminished the size of the characteristic clusters of crossed needles of $CaSO_3,2H_2O$. Colloids, however, retarded precipitation, and caused the calcium sulphite to separate as spherical granules, whose size increased with temperature, time, *p*H and the initial concentration of sulphurous acid. He found that the greater the amount of sulphur dioxide used the more complete was the precipitation of calcium sulphite on liming the hot juice back to a given *p*H. Farnell states that *p*H 6·8 is the figure employed in the white sugar factories of Natal and Mauritius. Though *p*H 8·6 for the hot juice is ideal as far as obtaining the optimum sulphite precipitation is concerned, the alkalinity is such as would make the juice somewhat dark in colour. This renders such a *p*H unsuitable for white sugar manufacture, but for the production of raw 96 per cent. sugar, the darkening is not so serious ; in fact, McAllep (*Intern. Sugar J.*, 1925, **27**, 382) has recommended *p*H 8·2 as corresponding to the best hydrogen-ion concentration of the hot juice on leaving the settling tanks in the Hawaiian factories. Farnell advocates liming to *p*H 7·6 to 7·8, at which sulphite precipitation would more nearly approach completion. Hartogh (*Archief Suikerind. Nederl.-Indië*, 1928, **36**, 1175) states that in the juice sulphiting operation, the sulphur dioxide should be passed until the *p*H is 7·1–7·2, and that syrup sulphitation should be controlled at *p*H 5·3–5·5. For this purpose, bromothymol-blue and chlorophenol-red respectively are employed.

In the South African refineries, heavy sulphitation is necessary. This introduces the difficulty of producing sugars substantially free from sulphur dioxide. The following procedure (*Proc. S. Afr. Sugar Tech. Assoc.*, 1930, 60) is advocated. The mixed juice is treated at 60°–70° C. with a small quantity of lime such that, when sulphited to 2,500 -3,500 p.p.m., its *p*H will not be less than 7. Then about 90 per cent. of the total lime is added, sulphited and a small excess of lime added to raise the *p*H to 8·3. Afterwards, phosphoric acid is added to *p*H 7·4–7·8, when the juice is heated to 98° and allowed to clarify for $1\frac{1}{4}$–$1\frac{1}{2}$ hours. The syrups are kept at about 55° Brix, heated to 80° and the suspended

matter is allowed to settle out ; their pH not being allowed to fall below 7·2.

Activated carbons, used in conjunction with the sulphitation processes, render rigorous pH control not so imperative, since they adsorb much of the juice acids (*vide* Mazzadroli and Vareton, *Zymologica*, 1929, **14**, 73).

Carbonation.

Purification by carbonation comprises the addition of lime-cream to the sugar solutions in large excess, followed by the passage through them of carbon dioxide to precipitate all the dissolved lime as calcium carbonate. The pH must not be allowed to fall to the point which will cause calcium carbonate to pass back into solution as the bicarbonate. The pH variation given in Fig. 169 for the neutralisation of carbonic acid with NaOH, which happens to be almost independent of the concentration of reactants except at the two ends, the dotted lines referring to more concentrated solutions of alkali, gives some idea of the pH change undergone in sugar solutions. The use of calcium hydroxide will produce a difference in pH during the neutralisation of the second half of the acid, due to precipitation, but not during the first half. From Johnston's (*J. Amer. Chem. Soc.*, 1915, **37**, 2001) data regarding the solubility of calcium carbonate in water in equilibrium with varying partial pressures of carbon dioxide, it has been calculated that for partial pressures of carbon dioxide ranging from 0·0002 to 0·0005 atmospheres, the pH of the solution in equilibrium with solid calcium carbonate varies from 8·4 to 8·1. As these pressures compare with those of carbon dioxide present in the air, it follows that these pH's are those at which calcium carbonate begins to precipitate. Assuming the sugar to have no effect on this pH it appears that carbonation must not be continued below pH 8·1 otherwise the precipitate will begin to redissolve. The pH range for magnesium carbonate for the same pressures is 9·6 to 9·5. Fig. 170 shows that pH 8·1 falls almost within the limits between which these processes should be effected. Sometimes carbonation is performed in two stages by restricting the first stage to pH 11–12 so as to precipitate and remove by filtration such non-sugars which tend to redissolve at lower pH's, *e.g.*, anthocyanin, pectins, and gums. Care, however, should be taken to avoid the elimination of sugar as tri-calcium saccharate, $3CaO,C_{12}H_{22}O_{11}$, which, though difficultly soluble in strongly alkaline solutions, will, if given time, redissolve.

Use of Ion-Exchange Resins.

Suggestions regarding the possible use of ion-exchange resins in sugar refining have recently been made. Thus Dymond (*Proc. 22nd An. Cong. S. Afri. Sug. Tech. Assoc.*, 1948, 74) has outlined a pre-clarification treatment of cane sugar juice, in which phosphoric acid is added to bring the phosphoric acid content of the juice up to 0·03 per cent. After passing sulphur dioxide until *p*H 3·2 is reached 3·5–8 lbs. of clay (per ton of cane) are added in order to precipitate wax, gums and protein matter. These are separated by filtration with the aid of 0·5 per cent. of " Hyfluosupercel " through resin beds. He claims that the advantage of this process over " lime-heat " clarification is that not only is it carried out in the cold but that more colloidal matter is precipitated than under alkaline conditions.

Fonseca (1949), however, describes a complete refining process. The cane juice is sulphited to *p*H 3·5 to 3·8, passed through a base-exchange resin and immediately treated with lime to *p*H 6·8–8·0. After heating, settling and decanting, the clear liquid is again passed through a similar type of resin, when it is evaporated to 55°–60° Brix. After mixing with 0·1 per cent. of filter-aid the syrup is filtered and crystallised.

Stability of Sugar.

The suitability of raw beet sugars for storage, according to Preininger (*Z. Zuckerind Czechoslov.*, 1929, **53**, 617), is better ascertained by *p*H measurements than by titratable acidity determinations. The sugar should be at *p*H 7 ; if between *p*H 7–8 it is unsuitable for long storage and if below *p*H 7 it is liable to inversion.

Automatic *p*H Recording and Control.

Some reference will now be made to the ingenious methods which have been developed for automatic *p*H reading and also for the adjustment of the alkalinity of sugar solutions. Balch and Paine (*Planter and Sugar Mfr.*, 1925, **75**, 347 ; *Intern. Sugar J.*, 1926, **28**, 425) found that for *p*H work a tungsten electrode in presence of manganic oxide worked satisfactorily in alkaline solutions. Such an electrode was found by Parker (*Ind. Eng. Chem.*, 1925, **17**, 737 ; U.S.P. 1,513,558/1924) to be capable of giving voltages when compared with a standard calomel electrode which could be calibrated in terms of *p*H (see p. 107, Vol. I). Fig.171A shows the arrangement used by Balch and Paine. The upper portion is a calomel electrode and the lower portion, into which dips the saturated potassium chloride " salt bridge " and

also the tungsten electrode, is the electrode chamber. The latter is made of a glass tube, coated at the lower end with Mn_2O_3 around which a tungsten wire is wound, one end passing through the glass tube containing mercury. Both electrodes are connected to a recording potentiometer. The sugar solution, its temperature having previously been regulated by means of cooling coils, was pumped through the electrode chamber. This apparatus could be made to give not only a continuous pH record during liming, but also a warning, by lights or bells, when the pH value was not

CALOMEL ELECTRODE

TO RECORDING POTENTIOMETER

"SALT BRIDGE"

TUNGSTEN ELECTRODE

Mn_2O_3 LAYER COVERED WITH COIL OF TUNGSTEN WIRE

ELECTRODE CHAMBER

COOLED SUGAR JUICE PUMPED IN
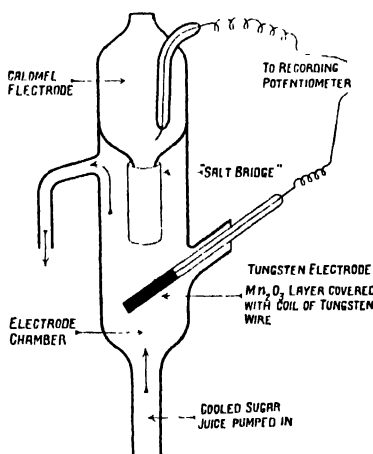
Fig. 171A. —Tungsten and Calomel Electrodes.

within the prescribed limits ; and by operating an electromagnetic valve, could be made to control the rate of lime addition (see also Parker, *Ind. Eng. Chem.*, 1927, **19**, 66).

Neither the quinhydrone, antimony nor tungsten-manganese sesquioxide electrodes were found by A. L. Holven (*Ind. Eng. Chem.*, 1929, **21**, 965) to be entirely satisfactory for the automatic determination of pH during the addition of lime, owing to their inability to hold their original calibration. Bare tungsten wire in conjunction with a calomel half-element was more suitable, though it necessitated the use of devices to counteract the effects of variations of temperature, viscosity, density and chemical nature of the products. Such an electrode has a temperature coefficient of o·002 volts per degree. The electrode is susceptible to poisoning. Holven concludes that though the electrometric method is more sensitive than the colorimetric method it offers no great advantage.

*p*H Survey of Sugar Cane Soils.

O. Arrhenius (*Java Archief*, 1927, **35**, 503) gives an interesting account of the methods adopted in the survey of the sugar-cane fields of Java with regard to the hydrogen-ion concentration of the aqueous soil extracts. Sugar canes thrive best in soils of about *p*H 7, and consequently a systematic investigation of the soils has been made in order that only those areas having suitable *p*H's should be used, it being uneconomic to correct, by adding lime, those soils which are more acid. Sampling is a matter of considerable importance, and for each test about 300 grams of soil were taken, placed in a muslin bag, dried, and after transference to bottles, were extracted with water and the *p*H estimated by means of Gillespie's " Drop Ratio Colorimetric Method."

The appearance of blight, caused by " frog hoppers," on the sugar cane in the West Indies has been attributed to soil acidity (Turner, *J. Agric. Sci.*, 1929, **19**, 26, 83).

*p*H and Sugar Beet Growth.

Soil suitable for growing sugar beet must be about *p*H 7·0 and unsatisfactory yields are obtained from soils below *p*H 6·0. In Ireland Crown Rot of sugar beet, a serious menace caused by *Phoma betae*, occurs in soils of *p*H 8 and above (Gallagher, *J. Dept. Agric., Dublin*, 1929, **29**, 61). From a consideration of the production of sugar beet in Southern Sweden, O. Arrhenius (*Ind. Eng. Chem.*, 1928, **20**, 219) found that maximum yields were obtained from soils of *p*H 7·0–7·5, 90 per cent. of the maximum at *p*H 6·5, and 80 per cent. at *p*H 6·0.

Glucose.

In the manufacture of glucose syrup from maize starch, the protein and other impurities may be flocculated from the converter-juice by means of an alkaline Fuller's earth gel, made by adding sodium carbonate to Fuller's earth, for the first stage of neutralisation of the acid-liquor. The Fuller's earth gel should be added above 80° until the *p*H has reached 3·5. The " floc " is then decanted (Segal, *J. Soc. Chem. Ind.*, 1934, **53**, 317T).

Fructose.

According to Dykins, Englis *et al.* (*Ind. Eng. Chem.*, 1933, **25**, 937, 1165), the best condition for the production of palatable fructose syrup from Jerusalem artichokes, without intermediate crystallisation, is hydrolysis with hydrochloric acid at *p*H 4·2 for 20 minutes at 130° F.

CHAPTER XXXVIII

THE IMPORTANCE OF HYDROGEN-ION CONCENTRATION IN PULP AND PAPER MANUFACTURE

THE production of satisfactory paper depends on the efficient adjustment of the hydrogen-ion concentration of the liquors employed. This applies more particularly to the sizing operations.

Much of the failure of manufacturers to realise that the acidity of the liquors should be controlled to a higher degree of precision than that obtainable by means of litmus, and very often by litmus papers, is shown by a certain lack of uniformity in the different batches of paper which have been manufactured in apparently the same way. Thus printers find that their type and plates deteriorate more readily when used on some papers than on others, although all were purchased as being of the same quality. The cause may generally be traced to the acid content. Such material, besides being of inferior quality, must have been subjected to treatment with too large a quantity of aluminium sulphate, some of which must therefore have passed out into the " backwater " and so have been lost. On the contrary, if too little aluminium sulphate be used there will be a tendency for some rosin size to remain undecomposed, and this again will lead to uneconomic manufacture. That litmus should have been selected by paper makers as the indicator for controlling the acidity of sizing solutions is somewhat remarkable, though not surprising, for, as will be shown later, its colour-change corresponds roughly to the pH range in which lies the smaller range necessary to secure good sized paper. The recent and precise methods for the determination of hydrogen-ion concentrations furnish means by which the acidities can be maintained within the narrower limits, now known to be imperative if the best papers are to be made, and incidentally limits which enable production to be carried out in the most economic manner, waste of aluminium sulphate and of rosin size being reduced to a minimum. In spite of this, it is felt that these methods are not being adopted as readily as they should be, probably due to some idea in the minds of paper manufacturers that they are uncalled for and are best left in the hands of physical chemists. It is probable, when printers come to realise how much of the efficiency of their work and how much the wear

of their type depend upon the acidity of the paper they employ, that they will include *p*H in their paper specifications. Another well-known disadvantage of acid paper is the decomposition and discoloration which occurs with age.

We shall now consider the various stages of paper manufacture, in so far as they lend themselves to *p*H control, and point out why such control appears to be necessary.

The first stage is to isolate the cellulose fibre from the raw material, namely, rags, esparto, various kinds of straw, coniferous woods, such as pine, spruce, poplar, and waste products, *e.g.*, paper, textiles, and jute bags, and then to convert them into pulp, sometimes known as " half-stuff." The preparation of pulp from any of these materials involves treatment with alkalis, sodium hydroxide or lime, of various concentrations, at different temperatures and usually under pressure. Linen and cotton rags, being of fairly pure cellulose, only require thorough washing by boiling with alkali and, when necessary, special treatment with malt to hydrolyse any starch which they may contain. This treatment, however, is not without its disadvantages, for it tends to soften the surfaces of the fibres and moreover to cause any precipitated ferric hydroxide and calcium carbonate to become embedded in the rags. Treatment with a slight amount of acid will dissolve out this foreign material, and at the same time slightly harden the surfaces of the rags. Too much acid effects too great a hardening, and unless the hydrogen-ion concentration of the liquors is suitably regulated such treatment may lead to disastrous results. The rust encountered comes from the iron in pipes and machines.

In recent years wood has become the most important source of raw material for the paper industry, and, indeed, also for its allied industry—that of artificial silk. Pine, spruce, and poplar woods are used. The lignified fibres of which they are composed, on being subjected to alkaline hydrolysis, undergo decomposition, the first material to become soluble being the non-celluloses ; and if the hydrolytic reaction be protracted the cellulose, which constitutes the cell-structures, also decomposes and then dissolves. After the removal of the bark, the wood is cut up into portions as small as possible so as to provide the maximum surface to enable the thorough penetration of the liquors. Two processes are available for the conversion of these chips into pulp : (*a*) the soda process, and (*b*) the sulphite process, the latter being more widely practised. In the " soda process " the chips are boiled with 6 to 8 per cent. solution of NaOH under pressure. Sodium sulphate is introduced which eventually becomes reduced to sulphide by means of the extracted organic matter.

Sulphite Pulp Process.

The " sulphite process " is of considerable importance, and though it involves the use of comparatively acid solutions, which render pH control difficult, it is surprising to find that investigations have shown that, providing the chips have had a satisfactory pre-treatment, the regulation of pH enables a more uniform and satisfactory pulp to be obtained. The process comprises the action of magnesium or calcium bisulphite liquors, saturated with sulphur dioxide, at a temperature somewhat above 100° C. and under pressure for many hours. The principle underlying the sulphite process appears to be the attack of bisulphite on the ketone groups present in the lignones, which renders the ligno-celluloses soluble. Neutral sulphites have a feeble hydrolysing effect ; their action does not become appreciable unless higher temperatures are employed.

Hägglund (*Papier-Fabr.*, 1926, 24 ; 1927, 24A) points out the great part which acidity plays during cooking. Escourrou and Carpentier (*Chimie et Industrie*, 1927, **18**, 13) have made a thorough study of the subject, and reference will now be made to their results. They consider that for the treatment of resinous woods pH measurements become of great importance. The initial absorption of the sulphite should be as complete as possible, and as it is primarily an adsorption process at the surface of the wood, it follows that before any reaction can ensue, the surface must be made as large as possible by cutting up the wood into the smallest sticks. The liquors should have penetrated thoroughly into the wood before 120° C. is attained. The value of a knowledge of the pH of the sulphite liquors, which can be found with indicators, will be apparent from Fig. 172, constructed from Escourrou and Carpentier's data. The two upper curves give the courses followed by the hydrogen-ion concentration of the liquors during 21 hours of cooking, the pressure being gradually increased during the first 6 to 8 hours to 4 kg. and thereafter maintained approximately at this pressure. Curve U is typical of the variations undergone in the production of unbleached pulp, whereas B represents the more careful control necessary to yield a pulp suitable for bleaching. The lower curves *u* and *b* give the temperatures (right-hand ordinate) attained during the runs corresponding to U and B respectively. The first sections of U and B correspond to the impregnation of calcium bisulphite liquors into the wood which, as the lower curves show, is accompanied by a steady rise in temperature. The slower rate of impregnation before 120° C. is reached permits of better disincrustation and also

of the liberation, on drying, of rose-coloured sulphonic acids, which are more susceptible to bleaching than those produced at higher temperatures. The lower *p*H during impregnation, though it promotes a slower action of the liquors, leads to a better product and one which is easy to bleach. If the *p*H, however, is kept too low the liquors may become black, resulting ultimately in a serious diminution in the yield of cellulose. The subsequent down-ward slope of both curves, showing that an increase in hydrogen-ion concentration occurred in the solutions, was due to the appear-ance of organic acids in the liquors through the dissolution of the lignified matter or incrustants. The temperature curves indicate
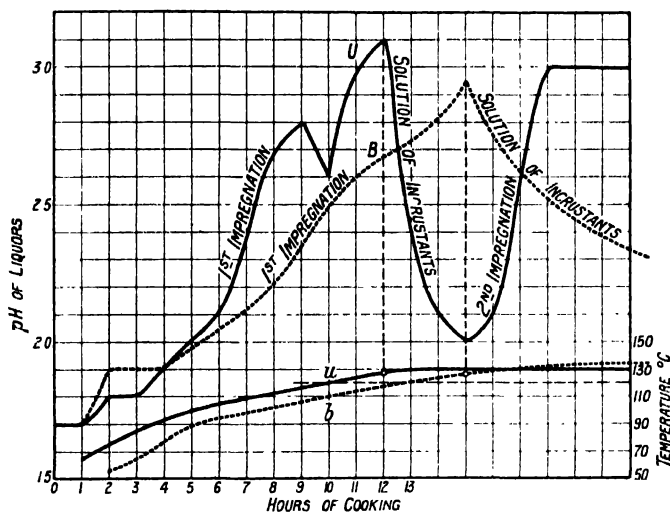
Fig. 172.—*p*H and Cooking of Sulphite Pulp.

that this solvent action started at a temperature a little below 130° C. Curve B shows a regular disincrustation attended by a progressive lowering in *p*H. After 27 hours' cooking, the *p*H of the escaping liquors had fallen to 1·8, and the pulp then obtained was soft and easily bleached. This appears to be usually the case. If the *p*H is above 2 the pulp is found to be hard, becoming harder with increasing *p*H, so that it can be bleached only with difficulty ; it is therefore put on the market as unbleached quality. If the initial impregnation is not thorough—which can be ensured by suitable regulation and control of the *p*H of the sulphite liquors—then the solution of the non-celluloses is partial, and in the course of cooking another impregnation action is set up,

as was the case in curve U. The• pulp corresponding with the top of the second impregnation curve is of "unbleached" standard.

During the cooking of ‚sodium-bisulphite cellulose with a solution of phosphoric acid and potassium phosphate, the lignin is converted by the acid sulphites into solid lignosulphuric acid, which eventually passes into solution. Hägglund (*Papier-Fabr.*, 1929, **27**, 165) has found that the rate at which dissolution occurs depends largely on the pH, the greater amount being dissolved at the lower pH values.

Bleaching.

Except for the lower grades of "newsprint," and the pulp designated for "browns," "wrappings," cardboards, etc., further drastic chemical treatment is given to the pulp. The process which has to be undergone by the wood and esparto "half-stuff" necessary for the manufacture of better-class papers, is one of bleaching. The "bleach" comprises, as a rule, a solution of bleaching powder, but on account of its slowness in bleaching, the bleaching liquor is very often rendered slightly acid by the addition of small amounts of dilute sulphuric or hydrochloric acid. This acid treatment is one which can be overdone ; thus too much acid will cause the evolution of chlorine, and also may convert some cellulose into oxy-cellulose which in impairing the fibre structure reduces the ageing properties of the resulting paper. Furthermore, bleaching action, being essentially one of oxidation, will tend to liberate acids by the interaction with the non-cellulose matter remaining in the wood-pulp, and if the amount of acid becomes too great, will cause the lignone groups to become chlorinated. Such chlorinated derivatives in the paper are highly deleterious. One advantage of having an acid-bleach, in addition to its enhanced efficiency, is that it dissolves out any insoluble calcium salts, *e.g.*, calcium carbonate. Another method of preparing the acid-bleach employed in recent years has been to pass chlorine into the alkaline pulp beyond the requirements of neutralisation. This is a process which demands careful investigation.

When chlorine is passed into water the following equilibrium is established :

$$Cl_2 + H_2O \rightleftharpoons HCl + HClO$$

and the bleaching action depends upon the ease with which the hypochlorite ion gives up its oxygen atom and thus becomes reduced to the chloride ion, *viz.*,

$$ClO' + 2H^{\cdot} \rightarrow Cl' + H_2O$$
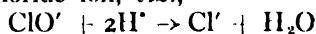
The normal oxidation-reduction potential, ε_0, of this reaction is $+ 1\cdot49$ volt, whence it follows that the effective oxidising potential, E, is given by

$$E = 1\cdot49 - \frac{RT}{2F} \log_e \cdot \frac{[Cl']}{[ClO'][H']^2}$$

$$= 1\cdot49 - 0\cdot058\,p\text{H} - 0\cdot029 \log_{10} \frac{[Cl']}{[ClO']}$$

It becomes apparent that the pH of the medium has a considerable effect on E and therefore on the oxidising capacity of the ClO' ion ; being greatest in strongly alkaline solutions. In acid solutions, however, [ClO'] is inevitably small, owing to small dissociation constant of hypochlorous acid, *viz.*, $3\cdot2 \times 10^{-8}$ (Britton and Dodd, *Trans. Faraday Soc.*, 1933, **29**, 537) and therefore the third term will have a relatively large negative influence on E. From pH $5\cdot5$ upwards the hypochlorite-ion concentration, on account of salt formation, increases. This, in conjunction with [Cl'], will minimise the effect of the third term on E.

Hisery and Koon (*Paper Trade J.*, 1936, **103**, 86, 980) observed that with chlorine, the best strength of bleached pulp is obtained at pH $1\cdot7$, but that the strength decreases with increasing pH ; the best colour for a given chlorine consumption is produced at pH $10\cdot8$. A good colour may also be obtained by acid bleach (pH $0\cdot8$–$3\cdot7$) if followed by treatment with calcium hypochlorite. There is a large consumption of chlorine at pH 6–7, probably owing to the initial neutralisation of the hypochlorous acid formed, *viz.*, at pH $7\cdot5 \mp 2\cdot0$. In bleaching pulp, a knowledge of the lignin content will give an indication of the amount of bleaching necessary. If large, a two-stage bleaching has been advocated : initially in acid solution with chlorine and finally at pH $10\cdot5$ with sodium hypochlorite. [See also, Samuelson, *World's Paper Trade Rev.*, 1936, 106.] Pascoe *et al.* (*Paper Trade J.*, 1936, **103**, Tappi, *sect.* 18) control the pH of the bleaching agent by suspending limestone in it in order to neutralise the acid liberated as the chlorine bleaching proceeds.

For the bleaching of Kraft pulps, MacLeod (*Pulp Pap. Mag.*, Canada, 1950, **51**, (3), 156) recommends the use of suitable mixtures of chlorine dioxide and chlorine at pH $8\cdot5$–$9\cdot5$.

According to Levy and Brennan (*Canad. Pat.*, 468037), chlorites may be employed to bleach pulp within the range, pH 5–$8\cdot5$, provided that a small amount of either a cobalt, nickel or manganous salt be present.

An automatic device involving glass electrodes and electronic apparatus has been described by Crawley (*Paper Ind.*, 1950, **31**, 1200), by which the pulp after chlorination is brought to a desired pH by the addition of lime.

The use of "antichlors" should be avoided, *e.g.*, sodium thiosulphate or sodium bisulphite, which, though eliminating the chlorine as neutral chlorides, may cause acids to be set free which will destroy the wires of the machines. It is preferable to wash the pulp free from bleach-liquors, or to use as antichlor *neutral* sodium sulphite, which releases no acids to attack the fibres.

Sizing.

As stated earlier in this chapter, the quality of a paper rests largely upon the manner in which sizing has been effected. After the half-stuff has been satisfactorily freed from extraneous chemicals, it undergoes mechanical treatment in water in a beating machine, where it becomes compressed into sheets and at the same time the fibres which protrude from the surfaces are removed. It is during this process that sizing operations are carried out in order that they may facilitate the matting together of the fibres to form sheets. Prior to 1807, the sizing agent used in the manufacture of papers for writing consisted of animal matter such as glue, but in that year Illig introduced rosin as a more suitable agent. To-day, rosin-sizing is generally adopted, though it should be mentioned that sizing with "water-glass" is finding favour for certain classes of paper. Rosin or colophony is the residue obtained after turpentine has been distilled off from the liquids which can be made to exude from the trunks of fir, pine, and other coniferous trees. Though it is, as may be expected, of somewhat variable composition, it is composed essentially of anhydrides of sylvic acid (abietic acid, $C_{20}H_{30}O_2$). The size is prepared by boiling the rosin for some hours with either sodium carbonate or sodium hydroxide solution, whence it dissolves to form sodium resinate, abietic acid, being a monobasic acid, thus $C_{19}H_{29}COOH + NaOH \rightleftharpoons C_{19}H_{29}COONa + H_2O$. The "equivalent" of the gum can be readily found by dissolving a sample in an excess of a warm standard alcoholic solution of sodium hydroxide, and then by titrating the excess of alkali with an alcoholic solution of an acid using phenolphthalein. Öman (*Papier-Fabr.*, 1926, **24**, Tech. Wiss. Teil, 410, 451) gives data which show that 100 grams of a typical rosin combined with 11·3 grams of NaOH, when titrated to cresol red, pH 8·0; 11·6 grams, using either phenolphthalein pH 8·5, or thymol blue, pH 9·0; and 11·8 grams, with thymolphthalein, pH 9·5. Had the rosin been pure abietic acid, it would have combined with 14·2 grams of NaOH.

A recent method of preparing rosin size is the so-called "Delthirna" process, in which the rosin is subjected to the action of

sodium hydroxide solution at ordinary temperatures. In such a method the contents of the water used, especially carbonates, may have a considerable effect on lowering the amount of rosin dissolved, and also the use of lower temperatures may be reflected in the colloidal condition of the resinate. The effects of the two sizes on the paper have been investigated by Hochberger (*Papier-Fabr.*, 1929, **27**, 83) and Strecker (*ibid.*, 99). According to the former author the *p*H of the aqueous extract of different papers sized by the Delthirna process varies from 4·5–5·8, whilst the corresponding values of ordinary papers are *p*H 5·5–5·8. The wider variation of papers sized by the Delthirna process is ascribed to non-uniformity of sizing.

The rosin size contains an excess of free rosin to an extent of from 15 to 25 per cent. If starch is not added to such a size before dilution with water, a milky liquid will be formed through the free rosin becoming colloidally dispersed. The agglomeration of rosin particles in the paper produces yellow specks. Sizes prepared with the aid of " atomisers " may, however, contain as much as 40 to 45 per cent. of free rosin. These sizes are added to the half-stuff in the " beater " during the last half of the beating process and then by interaction with a solution of aluminium sulphate, added either previously or subsequently, liberate rosin and alumina upon the surfaces of the fibres, and so cement them together. A well-known book on Paper Technology suggests that " the order of adding the sizing agents appears in many cases to have but little influence on the final result," but goes on to say that " in many mills it is customary to add a portion of the alum to the beater before running in the diluted size." The actual sizing operations should be carried out between *p*H 3·9 and 5·5 (*cf.* Roschier, *Pappers och Trävarutidskrift*, 1927, 154), and for this reason it seems probable that the addition of a part at least of the aluminium sulphate before adding the size is beneficial, for in reacting with any alkali left in the pulp it will tend to precipitate aluminium hydroxide, and this is known to begin to take place at *p*H 4·0 to 4·1 (Britton, *J. Chem. Soc.*, 1925, **127**, 2120). Roschier states that sizing does not take place below *p*H 3·9, which is evidently partly due to the fact that aluminium hydroxide is then under normal conditions not precipitated. Moreover, the rosin in the size begins to flocculate at about *p*H 3·7 and to rise to the surface of the solution. The ideal condition is to get the rosin in the size into a very fine suspension, so that it can be readily and evenly deposited upon the fibres. Too much acid increases the size of these particles and therefore gives rise to an irregular and defective sizing. It should be stated

here that abietic acid is insoluble in water. One would there-
fore expect that the rosin would be precipitated immediately an
amount of aluminium sulphate is added sufficient to neutralise
the alkali in the size, for the alkali contained in the size holds
some of the rosin-acid in chemical combination and a further
portion is probably peptised by means of the prevailing alkaline
reaction. This might be expected to occur at about pH 8.
Actually, however, visible precipitation does occur, owing to the
coagulation of some of the rosin present in a highly dispersed
colloidal solution. Precipitation occurs at about pH 3·7. The
transition from the disperse phase to the precipitate which occurs
with decreasing pH is accompanied evidently by an increase in
the size of the colloidal particles, which coagulate as soon as they
have acquired the magnitude requisite to stop the Brownian
movement which tended to keep them in colloidal suspension.
Hence, as Roschier states, the most satisfactory sizing conditions
are obtained at about pH 5, when the particles have acquired the
dimensions suitable for efficient sizing. It will be observed that
this pH lies about midway between the two extremes. Another
advantage obtained by adding some aluminium sulphate before
sizing is that it sets up automatically a pH (about pH 4) and so
prevents the precipitation of the curdy calcium resinates which
occur in alkaline solutions and thus impair the sizing.

Much controversy has taken place as to the actual mechanism
of rosin-sizing, whether the sizing is due to aluminium resinate,
or to rosin alone, or to rosin in conjunction with alumina. The
fact is that both alumina and rosin are deposited on the fibres,
but the query arises when the chemical condition in which they
were deposited is considered. The theory of sizing is of practical
importance, for when the constitution of the material deposited
on the fibre surface has once been established, it will then
become an easy matter to find the optimum pH conditions for
sizing. It cannot be merely a coincidence that the pH for
sizing should be above pH 4 and should preferably be about
pH 5. By analogy with some researches which the author has
carried out on basic aluminium salts, including basic aluminium
silicate (*vide infra*), it appears that such a pH range corresponds
to the precipitation of basic aluminium sulphate, which may per-
haps retain by means of weak chemical forces a little abietic
acid. *The extreme weakness of aluminium hydroxide as a base*, as
exemplified by the fact that it is precipitated at pH 4, *coupled
with the very weakly acid nature of abietic acid, render it highly
probable that only very little, if any, chemical combination could
take place between them, save perhaps a little which might possibly*

occur through the formation of a very insoluble aluminium resinate.
In a sizing process taking place above *p*H 4, it is unlikely that
any aluminium resinate would be contained in the precipitate on
account of the hydrolysing action which would then take place.
If combination occurred between such a weak acid and a weak
base by virtue of the insolubility of the salt produced, then that
salt would be precipitated from solutions more acid than *p*H 4,
and would undergo decomposition as soon as the *p*H of the
mother-liquor exceeded 4 (*cf.* Britton, *J. Chem. Soc.*, 1925, **127**,
2146). Roschier's (*loc. cit.*) contention that basic aluminium resin-
ate is produced at *p*H's below 4·5 appears therefore to be probable,
but it is improbable that aluminium resinate, $Al(C_{20}H_{29}O_2)_3$, is
formed at *p*H 5, and for that reason he considers that *p*H 5 gives
rise to best sizing. That this should be the *p*H requisite for
efficient sizing is probably due to the fact that aluminium
hydroxide then attains enhanced insolubility and therefore
becomes more firmly fixed to the fibres. The following equation
probably expresses the reaction which takes place in sizing :—

$$Al_2(SO_4)_3 + (6 - x)NaC_{20}H_{29}O_2 + (6 - x)H_2O$$
$$\rightarrow 2\,Al(OH)_{3-\frac{x}{2}}(SO_4)_{\frac{x}{4}} \downarrow + \tfrac{1}{2}(6 - x)Na_2SO_4 + (6 - x)C_{20}H_{30}O_2 \downarrow$$

Basic Aluminium   Free Rosin.
Sulphate.
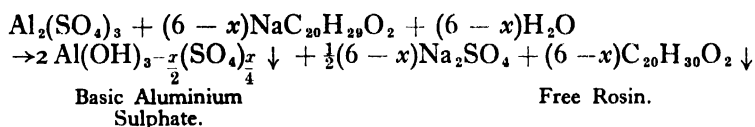
The actual value of x will depend upon the concentrations, the
method of mixing, and the temperature employed. Thus, in
the author's study of the precipitation of aluminium hydroxide
(*J. Chem. Soc.*, 1925, **127**, 2122) 5·7 equivs. NaOH were required
for complete precipitation, *i.e.*, $x = 0.3$. Whatever the true
explanation may be, sulphate is always found in the sized paper,
so also is rosin in the free state. Roschier recommends the range
*p*H 3·9 to 5·5 for sizing ordinary paper, and *p*H 5·8 for the sizing
of Kraft paper, which requires the minimum amount of rosin.
From what has been said it seems feasible to consider sizing as
being effected by the fixing to the pulp fibres of highly basic
aluminium sulphate, free rosin, and perhaps a little basic alu-
minium resinate. Several attempts have been made to prove that
aluminium resinate is precipitated by the interaction of sodium
resinate and aluminium sulphate, very often by estimating the
ash-contents of the dried precipitates ; but such experiments are
undoubtedly vitiated by the fact that the *p*H's which prevail are
those requisite for the separation of basic aluminium sulphate
and free rosin individually, and that simultaneous precipitation of
alumina and rosin must occur. Rosin, precipitated by acid or
obtained from alcoholic solution, is said to have comparatively

little sizing power, yet if alum is addèd after the alcoholic rosin
has been worked into the fibrous mass very good sizing results.
Price and Cameron (*Paper Trade J.*, 1946, **123**, Tappi Sect. 205A;
Price, *ibid.*, 1947, **125**, 256) claim that better sizing results if
sulphuric acid is used to adjust pulp slurries to pH 5 and they
recommend that rosin-size should be precipitated with solutions
containing both alum and sulphuric acid and not alum alone.
The scope of this chapter does not permit of a full discussion
of the theory of sizing; the reader is, however, referred to the
numerous papers by Öman in the (*Papier-Fabrikant, Tech.-Wiss.
Teil*, 1926–27).

Water-Glass Sizing.

The excellent monograph by Blasweiler (" The Use of Sodium
Silicate for the Sizing of Paper "; Constable, 1926) shows the
possibilities of silica-sizing. Like rosin-sizing, it is used in con-
junction with aluminium sulphate by adding to the half-beaten
pulp solutions of sodium silicate, which contain for each molecule
of Na_2O from 2 to 4 molecules of SiO_2. Sizing is often assisted by
using starch, and it is essential to work the sodium silicate well
into the half-stuff before the aluminium sulphate is added. The
curves given in Fig. 173 refer to some work of the author on the
reactions of silicic acid (*J. Chem. Soc.*, 1927, 425). One illus-
trates the pH changes undergone when a sodium silicate solution
is treated with hydrochloric acid, and shows that, although the
acidic nature cannot be satisfactorily represented in terms of a
dissociation constant, silicic acid has a weak, yet pronounced,
acid character. Though silicic acid is quite insoluble in water,
like abietic acid, it is not immediately precipitated, but passes into
a colloidal solution as soon as the alkali is completely neutralised.
The second curve shows that basic aluminium silicate and sulphate
are precipitated together at pH 4. It is exceedingly probable that
a similar curve would be obtained if rosin-size were substituted
for the sodium silicate. It is seen therefrom, that sizing, being
essentially due to the separation of a basic colloidal precipitate
within the meshes of the pulp, should be effected between pH 4
and 6, in an analogous way to·rosin-sizing.

Other stages in paper manufacture which may be influenced
by hydrogen-ion concentration are : (1) the introduction of filling
agents into the half-stuff, and (2) the colouring of the paper with
basic and acid dyes. The amount of filling (clays, etc.) which
can be satisfactorily adsorbed is dependent upon the amount of
alumina deposited upon the fibres. Roschier (*loc. cit.*) finds that
the best full-stuff from clay can be prepared at pH 5·0 to 5·5.

Briggs and Bull (*J. Phys.* *Chem.*, 1922, **26**, 845) state that the taking-up of dyes is a case of adsorption which varies with *p*H (*cf.* Speakman, *J. Soc. Dyers and Colourists*, 1925, p. 172 ; Scott, *Amer. Dyestuff's Reporter*, 1925, **14**, 862) ; and Theis (*Ind. Eng. Chem.*, 1925, **17**, 1165) claims that the maximum retention by clays of dyes is obtained at *p*H 4·0.
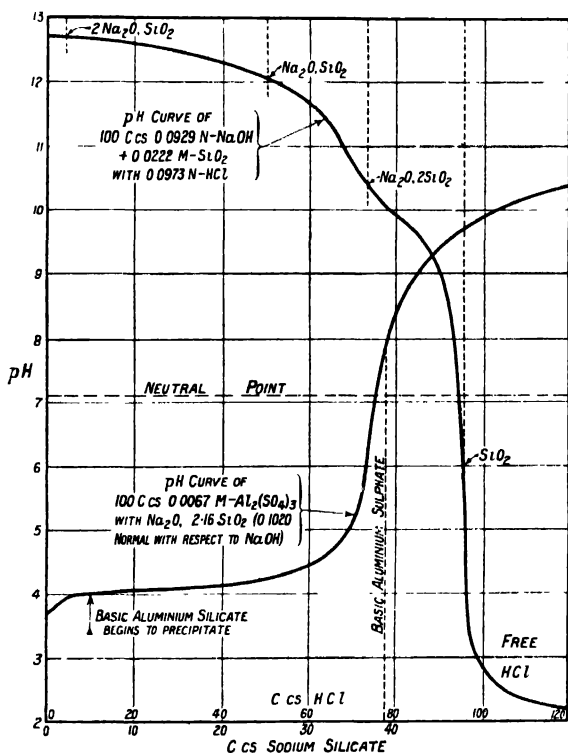
Fig. 173.—Graphs showing Acid Nature of Silicic Acid and Precipitation of Basic Aluminium Silicate.

Foaming troubles are sometimes experienced when sodium pentachlorophenate is used for the control of slime. Haefele (*Paper Trade J.*, 1948, **126**, Tappi Sect. 196) asserts that these troubles depend on the stock and can only be avoided by adjusting the *p*H to 6–7. As the salts of other chlorophenols and phenyl-phenol give rise to foam formation at other *p*H's it may often be possible to use one of them when sodium pentachlorophenate is unsuitable.

Determination of the Acidity and pH of Paper.

As will be understood, paper contains several potential sources of acidity, *e.g.*, sizing, loading and bleaching. The gradual liberation of acids within the paper results in its discoloration and deterioration with time. This acidity is harmful in wrapping papers, especially in respect to the damage which such papers may do to food and metal goods. Acid papers may also corrode printers' type and plates.

The pH values of papers have been found by Kalb and Falkenhausen (*Papier-Fabr.*, 1929, **27**, 330) to give some indication of the corrosive effects that they may have when kept in contact with metals in a humid atmosphere. Thus papers kept in contact with copper foil in an atmosphere of 90–95 per cent. relative humidity for 7–10 weeks were not corrosive if they had a reaction of pH 5 and above.

The total amount of acid in paper may be determined, according to the Paper Testing Committee of the Technical Association of the Pulp and Paper Industry (*Tech. Assoc. Papers*, 1932, 143), by extracting a known weight of mechanically disintegrated paper with boiling water and titrating the cold extract with N/100-NaOH to phenolphthalein. This " Tappi " method gives the total titratable acidity, but affords no information regarding the nature of the extracted acids. Edge, however, states that boiling does not effect a complete extraction of the acids from paper (*Proc. Tech. Sect., Paper Makers' Assoc.*, 1932, 82). Berndt (*Zellstoff und Papier*, 1935, **15**, 487 ; 1936, **16**, 15) finds that a hot extraction for one hour gives higher results than a 24-hour cold extraction, and Browning and Ulm (*Tech. Assoc. Papers*, 1936, 143) have shown that in carefully controlled aqueous extractions the weak acids appear chiefly in the first extracts, the strong acids passing into the subsequent extracts. Munds (*Papier-Fabr.*, 1936, **41**, 361) observed that the pH of a KCl solution extract is lower than that of a water extract.

Edge (*loc. cit.*) attempted to measure the actual pH of paper by extracting with water which had been adjusted to different pH values by means of N/100 acid or alkali ; allowing to stand for 24 hours in the cold, and measuring the pH electrometrically. When the pH of the extracting solution remained unaltered, Edge considered the pH of the paper itself to be the same as that of the solution. He also demonstrated by electrometric titration with the antimony electrode that it was necessary to have the paper present in the water throughout the titration.

The Specification for Papers (Unvarnished) for Electrical

Purposes issued in September 1936 by the British Standards Institution includes the electrometric determination of the *p*H of an extract obtained by boiling 100 c.c. of water with 2 grams of paper, cut into strips, 20 mm. by 3 mm. for 5 minutes. It also includes a standardised method of " spotting " papers with indicator solutions which have been half-neutralised with NaOH. Whilst such a method is not regarded as giving the *p*H of the paper, it is considered to indicate the upper and lower *p*H limits within which the actual *p*H of the paper lies. " Neutral " paper is regarded as being of *p*H 5·6, and indicators are so chosen that their *p*H ranges lie (*a*) below *p*H 5·6, (*b*) above *p*H 5·6, and (*c*) includes *p*H 5·6. Thus for neutral paper the colours of the indicator spots should be : bromophenol blue, *p*H 3·0–4·6, blue ; bromocresol green, *p*H 3·6–5·2, blue tinge ; bromocresol purple, *p*H 5·2–6·8, dirty yellow with no purple tinge ; phenol red, *p*H 6·8–8·4, yellow.

Burton (*Analyst*, 1938, **63**, 22) has devised a method in which 3 grams of paper are allowed to stand in contact with 100 c.c. of 0·1 M.-KCl for 48 hours with occasional shaking. The extract is decanted and the *p*H determined with the glass electrode. Boiling for one hour gave sensibly the same *p*H value. It is believed that this method gives the *p*H value actually prevailing inside the paper, the reason being that if paper can be considered as behaving analogously with gelatin, the *p*H inside gelatin is almost equal to that of the solution outside, when the solution contains an electrolyte such as potassium chloride.

Another method suggested by Burton is based on the method introduced by Atkin and Thompson (*J.I.S.L.T.C.*, 1924, **8**, 406) to estimate the *p*H prevailing inside leather. Various quantities of paper are inserted in 100 c.c. of 0·1 M.-KCl, and boiled for one hour, then cooled to 18° and the *p*H measured electrometrically. The *p*H values so obtained are plotted against the logarithms of the dilutions of the water in the original paper. For example, by placing 2 grams of paper, moisture content 8·6 per cent., in 100 c.c. 0·1 M.-KCl, the water in the paper is 0·172 c.c. and the dilution of the water in the paper is from 0·172 c.c. to 100·172 c.c., and is thus 100·172/0·172 = 582 times. The points so obtained lie approximately on a straight line and by extrapolation back to the logarithm of dilution 0, the *p*H value of the paper is obtained. Table 208 gives results obtained by this method and the extrapolated *p*H values are compared with those obtained by the B.S.I. method (2 grams of paper boiled with 100 c.c. of water for five minutes) and by the approximate indicator " spotting " method.

TABLE 208

Paper.	Moisture %.	pH.					
		2 grams.	4 grams.	6 grams.	Extrapolated.	B.S.I.	Indicator.
Light-coloured wrapping .	7·8	5·14	5·14	5·14	5·14	5·70	5·0
Dark-coloured wrapping .	8·6	4·70	4·70	4·70	4·70	4·60	— >
Blotting . .	6·2	3·85	3·56	3·34	1·0	3·90	3·0
White writing	5·7	4·06	4·02	3·98	3·60	4·32	3·7

Burton determines the total amount of acid in paper by carrying out glass electrode pH measurements on a series of extracts of a definite amount of paper with 0·1 M.-KCl solution, containing increasing amounts of alkali. By plotting pH against the alkali used, the amount of alkali required to bring the paper to pH 7 is found. The time allowed for each extraction is 48 hours.

THE IMPORTANCE OF HYDROGEN-ION CONCENTRATION IN BREWING

THE hydrogen electrode was introduced into the chemistry of brewing in 1913, when Emslander (*Kolloid Z.*, 1913, **13**, 156 ; *Z. gesamte Brauwesen*, 1914, **37**, 16), a former pupil of Freundlich, used it to investigate different beers. Even at that time much information was available regarding the part played by hydrogen ions in certain reactions which were promoted either by different enzymes, bacteria, or yeasts. Since Emslander's application of the hydrogen electrode, the concentrations of hydrogen ions set up at the different stages in the production of beer have received much attention. These physico-chemical researches have led to a very real advance in our knowledge of the mechanism of brewing, though it will be understood, when the difficulties presented by such a subject are taken into consideration, that these investigations, valuable as they are, constitute but the beginning of the developments in brewing chemistry along these lines. The results so far cbtained indicate how useful an index hydrogen-ion concentration may be of the most suitable conditions for carrying out such processes as " mashing," " boiling," and " fermentation," and also of the conditions most likely to be conducive to the maximum stability of the resulting beer. Hydrogen-ion concentrations of worts and beers are, however, largely determined by the various substances originally extracted from the malt, which may exert considerable buffer action. This tends to make pH control difficult, though it seems probable that, in order to obtain more satisfactory regulation of hydrion concentrations, efforts will have to be made (*a*) to modify the methods of malting, (*b*) to modify the process of mashing, and (*c*) to add suitable acids or bases to the worts.

Attention will now be directed to the parts played by hydrogen ions in the different processes involved in the brewing of beer.

Malting.

The first stage is the malting of the barley. The quality of the malt to be produced is predetermined to a great extent by the barley itself and the conditions under which it was grown and ripened. Malting comprises the artificial ripening of the corn

after steeping in water, germination, and its subsequent growth until the acrospire has grown to a height equal to about three-quarters of the corn. The diastase present in reacting with the superficial starch granules renders them soluble in water, chiefly as maltose, thereby loosening the main starch-containing portion, the endosperm, and so facilitating the enzymic reactions which eventually follow in the mash tun. If the growth be forced by the use of too high a temperature, the increased diastatic action required to render food available for the growing plant will result in an unnecessary loss of starch. After growth has continued for about a fortnight, and the endosperm has acquired a mealy consistency, it is arrested, and "withered," by heaping the malt for a period of 24 hours. The malt is then dried and cured in a kiln, the drying being effected by gradually raising the temperature while air is permitted to circulate through the kiln ; and the curing by maintaining a maximum temperature while only sufficient air is admitted for the combustion of the fires. It is during the latter stage that the flavour is developed, but great care must be exercised not to use too high a temperature, as this would seriously impair or even destroy the diastatic power. At the present time malting is carried out in an empirical way in accordance with the dictates of experience. It is certain, however, as the chemistry of brewing becomes more understood, that it will receive considerable investigation on account of the influence which the substances extractable from the malt have on the pH control which may be possible during brewing and on the ultimate stability of the beer. During malting the proteins undergo important changes and it is on these proteins, which pass into the wort, that the buffer action on the hydrogen-ion concentration depends.

Barley is enclosed by a membrane through which water can pass but which is impermeable to mineral salts. Chabot (*Bull. Assoc. Anc. Gand*, 1929 ; *Woch. Brau.*, 1929, **46**, 208) considers that this membrane is sufficiently weak at the embryo-end of the grain to enable the highly mobile hydrogen ions to gain access to the grain itself, and that this explains why a slight addition of acid, pH 6–7, to the steep-liquor slightly diminishes the absorption of water, and at the same time improves the colour, by making it paler, and the quality of the malt.

Cold-water extracts of green malt have been found by Lüers and Malsch (*Woch. Brau.*, 1929, **46**, 265, 275, see also Hopkins, *Biochem. J.*, 1929, **23**, 1022) to contain a protease and a peptidase. Protease acquires its maximal activity at pH 4·9 to pH 5·0, becomes quite inactive at pH 3, and at pH 8 its potency is about

one-quarter of its maximum value. The peptidase has its optimum at *p*H 7·5, is inactive at *p*H 4·5 and has only two-thirds of its maximum activity at *p*H 9. By means of electrometric titrations of malt extracts at various stages of the malting process, Hopkins and Kelly (*J. Inst. Brew.*, 1929, **35**, 402) have been able to follow the development of buffer action from *p*H 3·7 to *p*H 7·0. They consider that buffering between *p*H 3·7 and *p*H 4·3 is caused by peptones ; between *p*H 4·3 and *p*H 5·7 by amino-acids ; and between *p*H 5·7 and *p*H 7·0 by inorganic phosphates. These sections of the curves may therefore be taken as indications of the various enzymic activities (p. 322). In this way, slight changes only were observed to occur during steeping and the first stage of germination. During the following days of active germination there was rapid production of buffer substances, phosphates and proteins, but this was considerably reduced during withering and kilning. Steeping removed about one-half of the buffer substances originally present in the barley, with a consequent fall in *p*H. The development of buffers during germination is reflected in an increased *p*H value, which always falls during kilning. Though this work is of a preliminary nature, it opens up a promising mode of attack in controlling the all-important process of malting as regards the production of buffers in amounts that will enable suitable hydrogen-ion concentrations to be maintained during the subsequent stages of brewing. Incidentally the protein degradation products become more available as yeast nutrients.

Mashing.

After the malt has been suitably crushed into fine particles (not a powder), known as " grist," it is subjected to mashing, which in England takes the form of preparing an aqueous extract with warm water at about 65° C., *i.e.*, an " infusion," or when lager beer is to be produced, as is generally the case in Germany, this extraction takes the form of a " decoction," *i.e.*, after having made an initial extract by treatment with warm water, it is completed by boiling with the malt. In the English process, as much as possible of the soluble material which resisted extraction during mashing is obtained by " sparging " or spraying the malt with water at a higher temperature. The aqueous malt extract is known as " wort."

The production of soluble nitrogeneous compounds is at a maximum at *p*H 4·3 -4·7 at 50°. A somewhat high acidity favours the degradation of proteins, but the practical limit is at about *p*H 5·4 (Kolbach, *Woch. Brau.*, 1932, **49**, 369). In mashing

German malt with four times its weight of water, if buffered with lactates, the optimum pH for the formation of maltose changes from 4·4–4·6 at 30°, to 5·0–5·2 at 60°, to 5·8–6·0 at 70° C. (Windisch, Kolbach and Schild, *ibid.*, 246 ; Schmal, *Schweiz. Brau. Rund.*, 1941, **52**, 135).

Enzymes.

From what has been written it might be imagined that mashing is merely a physical process of dissolution of the soluble portions contained in the malt. This is not the case, for the majority of substances are insoluble in water, but they are rendered soluble by the action of the *enzymes* in the malt. Enzymes are colloidal in nature, and in composition they have points in common with the proteins. So far a few enzymes appear to have been isolated in the pure state in the form of crystalline proteins, *e.g.*, trypsin, pepsin and urease. In the pure state, they possess extremely potent enzymic activity. The majority of enzymes are, however, known to be present on account of the reactions which they accelerate. They are indeed catalysts, but the catalytic activity of each enzyme or ferment seems to be selective, being restricted to the decomposition of some particular organic body or " substrate." In common with catalysts they have large surfaces compared with their masses. Each enzyme has for its maximum activity narrow limits of hydrogen-ion concentration and temperature. Van Laer (*Ann. Brass. et Dist.*, 1920, **19**, 19, 23) argues that enzymes which enable compounds to hydrolyse, *e.g.*, the inversion of cane sugar, is merely a modification of the ordinary influence which hydrogen ions have, and that the enhanced activity is to be attributed to the high concentration of hydrogen ions adsorbed on the surface of the enzyme. Such a concentration will be in equilibrium with the hydrogen ions in solution, and, therefore, the maximum activity will be reflected in the pH of the solution.

We are now in a position to consider some of the reactions involved in mashing. Many are still unknown. In the first place the enzyme, diastase, in reacting with the complex starchy bodies converts them into simpler molecules of soluble starch. Now malt diastase appears to be able to do this in two different ways, by converting the starch somewhat indirectly into either dextrin or maltose. Windisch, Dietrich, and Beyer (*Woch. Brau.*, 1923, **40**, 49, 55, 61, 67) give the optimum pH for the former reaction as pH 5·03. Ohlsson (*Comp. rend. Soc. Biol.*, 1922, **87**, 1183) explains this dual power of diastase as being due to the presence of two distinct enzymes which he calls dextrino-

genase (giving rise to dextrin), and saccharogenase (giving rise to sugar), the former being destroyed at *p*H 4 and the latter at *p*H 10. The reaction which is needed in mashing is that of saccharification, and this is facilitated if the *p*H of the wort is about 4·4 to 4·5, which Sherman, Thomas, and Baldwin (*J. Amer. Chem. Soc.*, 1919, **41**, 231) have shown to be the optimum *p*H. Other workers' values range from 4·6 to 5·2 (Adler, *Biochem. Z.*, 1916, **77**, 150; Euler and Svanberg, *Woch. Brau.*, 1921, **38**, 111). The activity of diastase is in some way linked up with the neutral salts present, which are therefore designated as co-enzymes, for if they are dialysed out its activity becomes diminished, but it can be regained by the addition of acids or salts, though Sherman and Thomas (*J. Amer. Chem. Soc.*, 1915, **37**, 623) found that the maximum activity can only be regained between *p*H 4·2 and 4·6.

Another group of enzymes which play a very important rôle during mashing is the " phosphatases." They act extracellularly and liberate soluble inorganic or organic phosphates. Of the phosphates brought into solution, Adler (*Biochem. Zeitsch*, 1915, **70**, 1) found that as much as 93 per cent. was inorganic. He states that they are active at temperatures between 42° and 60° C., with maximum activity at 58° C., the *p*H being 5·4. The phosphate-content of wort is chiefly composed of a mixture of the primary and secondary acid phosphates of potassium, and the equilibria thus established exert a powerful buffer action corresponding to the second stage of the neutralisation of phosphoric acid from *p*H 6·0 to 7·6 (p. 298). One of the phosphatases, that are involved in the mashing reactions, is phytase, which accelerates the hydrolysis, optimum *p*H 5·2 at 48° C., of phytin, the phosphoric acid ester of the cyclic hexahydric alcohol, inositol, with the liberation of phosphoric acid. Other phosphatases of malt are glycerophosphatase, optimum 36°, *p*H 5·2, nucleotidase, optimum 49°, *p*H 5·6, saccharophosphatase, 41·5°, *p*H 6·0. These enzymes increase about tenfold during malting, especially if fairly long flooring at low temperature be allowed (*cf.* Luers and Malsch, *Woch. Brau.*, 1929, **46**, 143, 153). Inorganic phosphates depress the hydrolytic activity of phytase and almost completely inhibit it at 0·009 M. at *p*H 5·2 (Luers and Silbereisen, *Woch. Brau.*, 1927, **44**, 263, 273). According to Hopkins (*J. Inst. Brew.*, 1925, **31**, 399), the optimum *p*H ranges for the regulation of enzyme action in the mash-tub in order to obtain maximum yields are : (*a*) of extract, *p*H 5·1–5·2, (*b*) of sugar, *p*H 5·0–5·5, (*c*) of total nitrogen, *p*H 5·1-5·2, (*d*) of amino-nitrogen, *p*H 4·5–5·0.

During mashing much of the protein matter present in the malt undergoes hydrolysis (proteolysis) under the influence of malt proteolytic enzymes, of which peptase and tryptase are the more important. The following scheme, according to Schjerning, may be considered to show the course taken by plant proteins in passing from the insoluble condition with progressive hydrolysis through the colloidal stage to the comparatively simple soluble amino-acids :—

Insoluble → Albumin II → Albumin I → Peptones → Amino- → Ammonia
Protein   (Edestin)   (Leucosin)   Acids

Soluble albuminoids
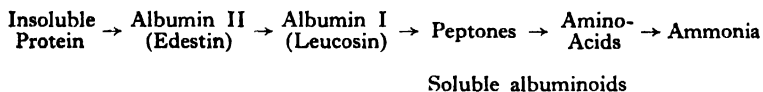
Such a scheme, however, is open to serious criticism.

In general, the hydrolysis of proteins, especially when brought about by the activity of enzymes, may be represented by the following stages :

PROTEIN —→ PROTEOSE —→ PEPTONE —→ POLYPEPTIDES —→
AMINO-ACIDS.
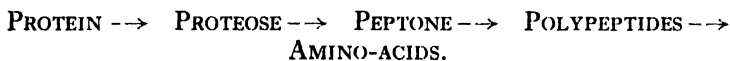
The class of proteins, known as the *albumins*, give colloidal solutions which coagulate on heating. The *proteoses*, of which albuminose is one example, give colloidal solutions, but they are not coagulable on heating. *Peptones* and *polypeptides* yield true solutions.

The passage of protein-decomposition products into the wort supply further buffer action, which thereby restricts hydrogen-ion concentration control. Dufour (*Pet. J. Brass.*, 1925, **33**, 1291) states that about 80 per cent. of the total buffer substances are extracted during the preliminary stages of mashing, though an increase in buffers is found to result from " sparging." It is for this reason that a greater command over the concentrations of the buffer substances which will eventually become extracted can be procured only by altering the malting procedures. The pH most favourable for the hydrolysis of polypeptides obtained from malt proteins occurs at 4·4 to 4·5, but the temperature required is just above 40° C., which happens to be unfavourable to diastase (Lundin, *Biochem. Zeitsch*, 1922, **131**, 193). Peptase, whose optimum pH lies between 3·7 and 4·3 in the case of kilned malt, and at 3·2 for green malt, converts leucosin into proteoses, peptones and denuclein, whereas tryptase, which brings about continued hydrolysis to amino-acids and ammonia, gives its maximum activity at pH 6·2 to 6·4. Parsons (*J. Inst. Brew.*, 1924, **30**, 30) gives pH 5·4 as typical of worts prepared by the English infusion process of mild ale, and 5·0 as the pH of a wort of bottling stout. As will be shown later, the existence of nitrogenous matter

in beer wort is of fundamental importance in that it supplies nutrients for the yeast, and also colloidal particles of such fine dimensions as to assist in " head retention." Protein matter, not sufficiently hydrolysed to give substances which pass into true solution, may give clear beers, though they contain colloidally-dispersed particles which on standing coagulate to form " haze." Sudden changes in temperature may also result in the formation of " haze." Moreover, the stability of the beer is, to a great extent, a question of nitrogen-content in that, by supplying nutriment to any yeast or bacteria which the beer may contain will tend to set up fermentation and putrefaction.
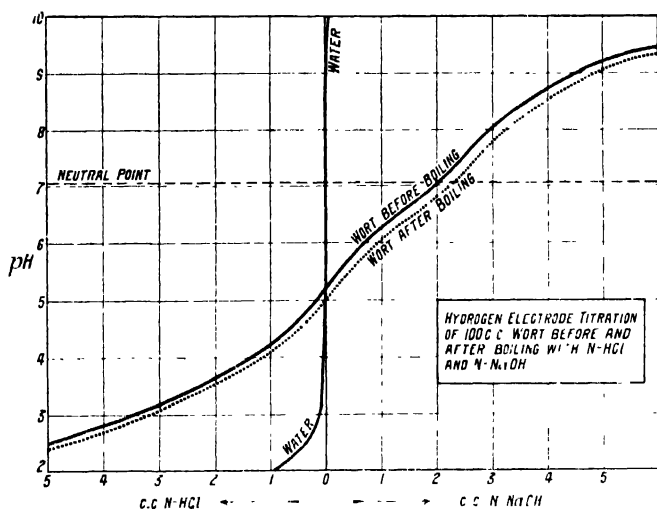
FIG. 174.—Curves showing the Buffer Action of Wort.

Fig. 174 gives an electrometric titration curve, obtained by Hagues (*J. Inst. Brew.*, 1927, **33**, 262) with the hydrogen electrode, of 100 c.c. of beer wort with N-sodium hydroxide and N-hydrochloric acid. By comparing this curve with the one marked " water," which represents the changes in *p*H when N-acid and alkali are added to 100 c.c. of distilled water, the buffer action of the phosphates and organic bases present in the wort will become apparent. This unboiled wort, which may be taken as representative of worts in general, had a *p*H of 5·2. On adding alkali, the hydrogen-ion concentration, instead of suddenly becoming very small, as in the case of water, suffered a relatively small diminution, as shown by the very small *p*H change. This particular buffer action over the *p*H range 6 to 7·6 is largely due

to the phosphoric acid in the wort being subjected to the second stage of neutralisation. The buffer action set up on adding acid is due to the presence of basic nitrogen groups, *e.g.*, — NH_2, in the protein decomposition products. It is noteworthy that the buffer substances in the wort are such as to produce no pronounced inflexion. This is evidently due to the presence of weak bases, and moderately weak acids, whose neutralisation curves coalesce. For further information concerning such a possibility, the reader is referred to Chapter X.

Titration of worts and beers " by stages " is being increasingly adopted as it is considered to indicate the amounts of the various buffering substances that come into play over different pH ranges. Kolbach (*Woch. Brau.*, 1929, **46,** 91) considers that by titrating worts before and after treatment with baryta, from pH 5·67 to pH 7·07 a measure is obtained of the amount of phosphates ; whilst above pH 7·07 the protein degradation products may be accurately estimated by the formol titration. The cause of buffering below pH 5·67 is considered as unimportant, though the extent of the buffering is important for it becomes involved in the fall in pH that occurs during fermentation. For titrations Emslander (*Woch. Brau.*, 1929, **46,** 407) employs a gold electrode, plated with iridium, and coated with platinum black. With the electrode just dipping into the wort, equilibrium is rapidly attained. He titrates to pH 4·5, 6·8, 8·3 and 9·18.

It will be seen that pH 4·4, which may be indicated by methyl orange, corresponds approximately to that degree of acidity which promotes the maximum activity of the chief malt enzymes. Hence it might be considered that this is the pH that should be aimed at in mashing. The aim of mashing, however, is to produce a wort which contains the maximum amount of fermentable matter, *e.g.*, sugars, together with an adequate amount of nitrogenous material for use in the subsequent fermentation. Although the optimum pH for the conversion of malt starch into soluble products with the aid of diastase is pH 4·4, it happens that at such a low pH saccharification becomes difficult, so much so that it becomes completely inhibited when the pH is slightly lowered. As far as the author has been able to ascertain, the most suitable range for wort production lies between pH 5·0 and 5·5.

Varying small proportions of substitutes for malt are introduced into the wort either by the action of enzymes or by simple solution. Of the former may be mentioned corn, unmalted barley, rice, rolled maize and of the latter, various sugars such as cane sugar, invert sugar and glucose. The glucose is usually manufactured from sago, maize and rice starches under the in-

fluence of sulphuric acid, due regard being paid to hydrogen-ion concentration.

The question of the effect of temperature on the diastatic activity in both decoction and infusion mashing has been investigated by Windisch, Kolbach and von Benedek (*Woch. Brau.*, 1929, **46**, 345). They found that at 50° the optimum is at *p*H 4·8 ; at 60° at *p*H 5·1 ; and at 70° at above *p*H 5·6. These figures refer to the fermentable extracts ; if the total extracts be considered the optima are all about 0·1–0·2 *p*H unit lower. Similar conclusions have been arrived at by Hopkins (*J. Inst. Brew.*, 1925, **31**, 399) and Windisch, Kolbach and Banholzer (*Woch. Brau.*, 1928, **45**, 523). The latter workers studied the influence of acidification, by hydrochloric acid or lactic acid, of malt mashes on the composition of the resulting worts. The maximal extract was obtained at *p*H 5·1, though the optimum *p*H as far as the fermentable extract was concerned was *p*H 5·5 and for apparent maltose was *p*H 5·2. They explain these differences on the grounds that more protein decomposition products are extracted between *p*H 5·5 and *p*H 5·1, whilst between *p*H 5·2 and *p*H 5·5 non-fermentable dextrins are also extracted. Below *p*H 5·2–5·3 acidification resulted in a marked diminution in attenuative capacity to an extent that rendered acidification inapplicable. Acidification of the mash led to increased quantities of phosphate and protein-decomposition products which acted as buffers. After fermentation, these acidified worts yielded beers whose reaction was similar to that obtained from untreated worts.

A colorimetric method of determining the *p*H values of wort has been introduced by Kolbach (*Woch. Brau.*, 1929, **46**, 305), and is claimed to be accurate to 0·05 *p*H unit. He also emphasises the need of eliminating errors caused by neutral salts in colorimetric determinations of *p*H. To compensate for the neutral salts in the wort, he recommends the addition of NaCl (conc. = 0·1 N.) to the reference buffer solution. The indicators advocated by Kolbach (*Woch. Brau.*, 1932, **49**, 81) are bromo-cresol green for *p*H 4·0–4·8 ; methyl red, *p*H 4·8–5·6, and bromo-cresol purple for *p*H 5·6–6·4.

Boiling.

The next stage in the manufacture of beer is " boiling," during which the requisite quantity of hops is added to the wort, and the wort becomes sterilised and concentrated. Boiling destroys the enzymes, causes a little caramelisation of the sugars and assists in the extraction of the rosins from the hops. The

production of caramel required for dark beers is accomplished more easily in alkaline solution. Another important point is that boiling causes the coagulation of some of the albumins, which were in the wort in a condition of unstable colloidal suspension. The partial coagulation of the proteins is known technically as the " break " ; in it, hydrogen-ion concentration undoubtedly is an important factor. Lüers (*Z. gesamte Brauwesen*, 1920, **43**, 51) states that the best " break " is obtained at pH 5·2 (*cf.* Hopkins, *J. Inst. Brew.*, 1921, **27**, 401, and Hagues, *ibid.*, 1927, **33**, 262). Windisch, Kolbach and Vogl (*Woch. Brau.*, 1929, **46**, 403) give pH 6·2 for one hour's boiling, and pH 5·5 after five hours' boiling. There is a tendency for the coagulum to become less in quantity with increasing acidity, perhaps through salt formation with the colloidal protein matter, or in the case of prolonged boiling to partial hydrolysis of the proteins. Hagues (*loc. cit.*) found that at pH's higher than 5·0 the size of the particles of the coagulum is the same and appears to be independent of pH ; on the acid side the size rapidly diminishes with increase in acidity. The pH at which particle-size suddenly becomes sensitive to hydrion concentration, though not sharply defined, lies, according to Hagues, in the region of pH 5·0 or 5·1. The fact that only 6 per cent. of the nitrogen-content of wort is coagulable on boiling gives some idea of the proportion of protein colloidally dispersed in the wort. It is often said that some of the coagulum re-dissolves on continued boiling, some of which may probably be precipitated from the finished beer on ageing. Some of this redissolution may be due to hydrolysis of the protein particles into small particles which tend to approximate in size to molecules in true solution. It seems more than a coincidence that the condition most suitable for " breaking " should be at pH 5·0, for it will be recalled that this is not far removed from the iso-electric point, *viz.*, pH 4·7, of many proteins at which they possess their minimum solubility.

Another point which undoubtedly has some effect on the " break " is the reaction which ensues between the tannic acid liberated from the hops and the proteins. This problem has been attacked by Emslander (*Pet. J. Brass.*, 1928, **36**, 1292, 1318, 1345) who studied the tanning action of tannin on gelatin. Surface tanning of the gelatin took place most strongly from tannin solutions at pH 6·46. Diffusion of the tannin into the gelatin occurred at other pH values, with optima at pH 4·5 and 9·18. It was considered that the most suitable pH for wort boiling with hops would be 4·5, but such a pH value is never obtained. Surface tanning of the proteins in wort is usually avoided by the

gradual addition of hops in small quantities. Emslander contends that the pH of the wort, on account of the tanning action, has a pronounced effect on the flavour of the wort, and moreover that pH variations are responsible for differences in colour of the wort. He thinks that the colouring matter accompanying hop tannin is related to quinone, which colouring matter, depending on the reaction, undergoes oxidation on exposure to air, and so, like quinone, darkens in colour.

From electrometric curves of worts and beers with alkali, it can be ascertained at what pH they possess their greatest buffering. Emslander (*Woch. Brau.*, 1933, **50**, 89, 102, 108, 119) stresses the need to determine the pH of maximum buffering of hop samples and to employ just those samples which give the best precipitation of protein material. Best hops are most richly buffered at pH 6·7.

Humulone, the principal bitter acid in hops, is more stable in a medium of low pH in which the rosins are formed but slowly. In beer at pH 4·3 humulone is soluble to the extent of 14 mg. per litre. Beers therefore obtained from relatively acid worts usually have a pleasing mild hop bitterness. The colouring matter of both hops and malt is more soluble in media of high pH and consequently a high pH of wort and hop sparge tends to impart a deep colour to the beer.

Boiling is generally accompanied by a slight increase in acidity. This will be seen from the lower curve, in Fig. 174, which illustrates Hague's titration of a boiled wort. The wort is then cooled in refrigerators.

Fermentation.

The boiled wort is now subjected to the fermentative action of yeast for periods of usually a week's duration at temperatures increasing from 15° to 20° C. This process may give rise not only to the formation of alcohol but of small amounts of glycerol, fusel oil, succinic, acetic, formic, and other acids and carbon dioxide. Various aldehydes and esters have been detected.

The complex nature of yeast leads to many and varied reactions. Perhaps the more important enzymes in yeast are invertase, maltase, and zymase. The function of the first two is to convert disaccharoses, *e.g.*, sucrose, maltose, into monosaccharoses, such as dextrose, and the zymase converts these monosaccharoses into alcohol and carbon dioxide. Among the factors which contribute to the activity of yeast are (1) the nutrients present in the wort, *e.g.*, nitrogenous products, which have undergone sufficient hydrolysis to form molecules of such magnitude as to enable

them to diffuse through the cell walls, ⟨2) phosphates, and (3) the hydrogen-ion concentration. Harden and Young (*Proc. Roy. Soc.*, B., 1908, **80**, 299) observed that when a phosphate was added to a fermenting mixture of dextrose and yeast juice there occurred an increase in the rate at which fermentation proceeded, and moreover, an increase in the amount of fermentation. They concluded that phosphate was probably necessary for the action of yeast, and postulated that the following equation might express the main reaction involved in alcoholic fermentation :—

$$2C_6H_{12}O_6 + 2K_2HPO_4 \rightarrow 2CO_2 + 2C_2H_5OH + C_6H_{10}O_4(PO_4K_2)_2 + 2H_2O$$
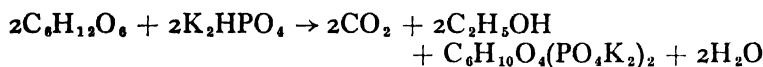
(see however Kluyver and Struyk, *Proc. K. Akad. Wetensch.*, Amsterdam, 1926, **29**, 322).

The hexose-diphosphate was believed eventually to hydrolyse back to dextrose, which reaction according to Euler and Nordlund (*Z. physiol. Chem.*, 1921, **116**, 229) is the slower one, and therefore determines the rate of fermentation. They consider that a co-enzyme is necessary. Euler and Tholin (*Z. physiol. Chem.*, 1916, **97**, 269), working with dried and living yeast, found that K_2HPO_4 accelerated fermentation, as indicated by the evolution of carbon dioxide, to a great extent at pH 4·5, but at pH 8 it retarded the gas liberation. Albers (*Z. physiol. Chem.*, 1935, **235**, 47) considers that the " top " and " bottom " yeasts contain different phosphatases ; that in the " top " yeast breaks down hexose diphosphate at an optimum pH of 3·5, whilst that in the " bottom " yeast is most active at pH 7. The action of invertase in fresh yeast on cane sugar in presence of K_2HPO_4 attains a maximum at pH 4·5. The activity of maltase of living yeast is prevented at pH 8 (Euler and Emberg, *Z. Biol.*, 1919, **69**, 349). Svanberg (*Z. tech. Biol.*, 1920, **8**, 1) finds that the optimum pH range for the growth of yeasts, whether grown in beer worts or in solutions containing ammonium salts and phosphates, is for (*a*) top yeasts, pH 3 to 6, as used in worts prepared by infusion, and (*b*) bottom yeasts, pH 4 to 6, for decoction worts. Zikes (*Zentralbl. Bakt.*, II., 1919, **49**, 353) finds 25° C. to be the optimum temperature. There appear to be many conditions which determine the best hydrogen-ion concentration for fermentation. Thus Emslander (*Z. gesamte Brauwesen*, 1919, **42**, 127, 135) suggests that it should correspond to pH 4·5 for worts brewed in carbonate waters, and to pH 4·2 for worts obtained from gypseous waters ; Van Laer (*Pet. J. Brass.*, 1922, **30**, 887) considers that the presence of antiseptics, *e.g.*, hops, has some effect ; and Fodor (*Fermentforsch.*, 1920, **3**, 193),

Euler and Heintze (*Arkiv. Kemi Mineralogi*, 1917, **7**, 5, 21), and Euler and Emberg (*Z. Biol.*, 1919, **69**, 349) believe that the optimum pH depends upon the colloidal nature of the different yeast enzymes, the amphoteric substrate, and particularly upon the difference in acidic nature between these colloids and their respective substrates. It is probable that these points accord with Warden's (*Amer. J. Physiol.*, 1921, **57**, 454) contention that alcoholic fermentation is the outcome of catalytic actions on the surfaces of yeast cells, and is therefore due to the considerable amount of adsorption which must take place either on the cell walls or on the colloidal particles in the yeast juice.

Regarding the optimum pH for the process of fermentation, other points are worthy of attention. It is an interesting fact that both enzymes and yeasts, when in preponderating amounts, tend, through the development of certain buffer agents, to set up pH values at which they possess maximum activity. During brewing, beer is very apt to be infected with bacteria and wild yeasts from the atmosphere. Among the bacteria sometimes found in beer may be mentioned *Saccharobacillus pastorianus*, which may give rise either to a bitter taste or to turbidity, *Bac. viscosus*, which may produce " ropiness," and *B. acetoethylicum*, which causes the formation of acetone. Hydrogen-ion concentrations may, however, be so adjusted that these bacteria and yeasts can thrive only with great difficulty, and fortunately it happens that the desirable pH, *viz.*, pH 4·5, for normal fermentation is too low for their reproduction, though it is not entirely prevented. Van Laer (*Comp. rend. Soc. Biol.*, 1922, **87**, 990) gives the optimum pH for the growth of the first two as pH 6·8 in hopped wort and pH 5·5 in unhopped wort, and Arzberger, Peterson, and Fred (*J. Biol. Chem.*, 1920, **44**, 465) find pH 5·8 to 6·0 for the last.

Some interesting observations were made by Trantwein and Wassermann (*Biochem. Zeitsch*, 1931, **236**, 35 ; **240**, 423), who investigated the rates of fermentation and respiration of " top " and " bottom " fermentation yeasts which were allowed to grow in a 20 per cent sucrose solution, buffered with phosphate. Whilst the " top " yeast fermented more rapidly than the " bottom " variety, the curves correlating fermentation and pH were closely similar. The optimum pH was about 4·5, a steep rise occurring just below pH 2·7 and this was followed by a more gradual rise to pH 4·5. This was followed by a steady diminution in the rate of fermentation, which diminution became rapid at pH 6·5. Above pH 8 no fermentation occurred. Respiration followed a similar course, with the difference that its decrease with rising pH was more gradual. It remained constant at pH

10·75 and ceased at pH 11·85. Respiration thus takes place above pH 8 without leading to fermentation.

The fermentative activity of yeast alone has so far been considered, but in order for fermentation to proceed satisfactorily it is also necessary that fresh supplies of yeast should be reproduced. This the yeast does, during the fermentation of the wort, by living on the assimilable nitrogen and other nutrients which may be present. Protein-matter in the wort is assimilated by the yeast as the result of proteolysis caused mainly by the enzymes, pepsin, tryptase, and ereptase of the yeast. Thus yeast-pepsin converts proteins into peptones (optimum pH 4·45), which, together with polypeptides, are then with the aid of yeast-ereptase degraded into amino-acids (optimum pH 7·8), whereas yeast-tryptase hydrolyses albumin, gelatin, and casein into polypeptides and amino-acids, the optimum pH being 7. Hence, according to Dernby (*Biochem. Zeitsch.*, 1917, **81**, 109) the optimum pH for proteolysis as a whole, *i.e.*, autolysis, is 6·0 to 6·2, and the limits between which such decomposition is possible are pH 4 and 7. The question now arises whether the wort contains enough nitrogenous matter to support the life of the yeast, and in regard to this Hulton (*J. Inst. Brew.*, 1922, **28**, 4) states that even in worts containing the lowest amounts there is always a sufficiency.

According to Hagues (*J. Inst. Brew.*, 1928, **34**, 362; 1929, **35**, 51 ; see also Windisch, Kolbach and Schild, *Woch. Brau.*, 1930, **47**, 327, 337) the initial fall in pH during fermentation is caused, not by the development of acidic substances, but by the assimilation by the yeast of some of the buffering substances. For the reproduction of yeast there are two optima, pH 4 and pH 8·5, which happen to correspond with the optimum activity of pepsin and ereptase respectively. As regards the composition of beers very little difference appears to exist between the beers brewed from worts of pH 4–8, and consequently it is probable that varying pH has very little effect on the course of fermentation within this range. Nevertheless, keeping the pH of beers low has been found by McCandlish and Hagues (*J. Inst. Brew.*, 1929, **35**, 61) to enable a better separation of the yeast to be made, and to maintain the yeast in a good condition for longer periods than is otherwise possible.

Beer Stability.

Proteins and protein derivatives in beers exert buffer action, which tends to maintain a high pH, and thereby renders the beers more vulnerable to the attack of wild yeasts and bacteria. Hence the problem of beer stability has come to be associated with

the nitrogenous content. Fömslander (*Z. gesamte Brauwesen*, 1914, 37, 164) holds that, the greater the amount of protein the less the stability, and Fernbach (*Ann. Brass. et Dist.*, 1923, 21, 289) believes that yeast does not remove a sufficient amount to ensure stability. It is evident that this problem must be referred back to the malting process and the development of amino-nitrogen which occurs during the germination of the barley (Moritz and Fuller, *J. Inst. Brew.*, 1926, 32, 602). The reaction corresponding to stable beers, *viz.*, about *p*H 4, is very unfavourable to the development of the different races of *sarcina* (a most serious group of beer disease organisms) which have different optima for their growth. The growth of some races is most rapid between *p*H 5·7 and 6·4 though some have an optimum at *p*H 5·3. It is often found that beers, brewed from malts which saccharify badly, and which have fermented sluggishly, frequently have their *p*H well within the danger zone (Stockhausen *Woch. Brau.*, 1925, 42, 19, 25, 31, 37, 43 ; Stockhausen and Stege, *ibid.*, 240, 253, 261, 268). Stockhausen gives the *p*H range 4·0 to 4·5 for stable beers, while Parsons (*J. Inst. Brew.*, 1924, 30, 30) regards *p*H 4·15 as the " safety point " for beers at " racking," beer on the acid size of this value remaining sufficiently free from bacterial activity for trade purposes. Hopkins and Fraser (*ibid.*, 1928, 35, 387) discountenance the idea of a *p*H safety limit because there are several other disturbing factors, though McCandlish and Hagues (*ibid.*, 1929, 35, 61) consider *p*H 3·7–4·0 as such a range, especially if the beer is buffered in that zone.

The antiseptic power of hops is dependent on the hydrogen-ion concentration. Fernbach and Stoleru (*Ann. Brass. et Dist.*, 1924, 23, 1) found, from a study of their effect on the development of lactic acid producing organisms in *Bac. Delbruckii*, that the antiseptic activity was greatest between *p*H 5·5 and 6·8, had almost disappeared between *p*H 7·4 and 8·4, but at *p*H 8 the organisms were able to flourish in the hop decoction. Windisch, Kolbach, and Schüren (*Woch. Brau.*, 1925, 44, 285, 297, 309, 324, 335, 345) have made an extended research into the antiseptic power of hops and found it to reside largely in the humulone which they contain and to be a maximum at *p*H 4·3, the average reaction of beer. Hence, it appears that care must be taken that the beer should have the requisite acidity, though not sufficient to become apparent to the taste, and in order to ensure the maximum preservative action of the hops, the ratio of the hop-rate to acidity must be satisfactory. Dietzel (*Kolloid Z.*, 1926, 40, 240) was unable to trace any parallel relationship between acid flavour and hydrogen-ion concentration.

M

Brewing Water Treatment.

There is no doubt that much of the quality of beer depends upon the water, and many attempts have been made to ascertain whether adjustment of the pH results in an improved wort and one containing an increased amount of malt extract. As might be expected, the different compositions of natural waters have also an important effect, and in consequence the views recorded on the question are somewhat conflicting. Perhaps one of the views having valuable practical bearing is that of Poulsen (*Woch. Brau.*, 1925, 42, 91), who states that using calcareous water the pH of the brewing mash in a Carlsberg brewery has, since 1912, been adjusted by means of lactic acid developed in the mash by cultures of *Bac. Delbruckii*. He states that as the result of such a treatment a paler and a better flavoured beer is obtained, greater brilliancy is ensured, a better " break " having been obtained. Hagues (*J. Inst. Brew.*, 1926, 32, 8) and Petit and Raux (*Ann. Brass. et Dist.*, 1927, 25, 232) find that increased and better extracts are obtained by correcting the water with sulphuric acid, which on boiling give superior " breaks."

McCandlish and Hagues (*J. Inst. Brew.*, 1929, 35, 61) adjust the pH of brewing water to 7 by dripping sulphuric acid into the water as it passes into the mash-liquor tank ; pH values below 7 may result in tank corrosion. According to Caprino (*Zymologica*, 1930, 5, 47) water for making beer of the Pilsen type should be treated with lime-water and then sufficient hydrochloric or sulphuric acid to neutralise to 1 or 2 degrees of hardness. The optimum pH is 5·2, at which the most rapid and complete saccharification is obtained. Investigations into the variations of the pH of brewing water with reference to malt and barley extractions have been made by Chabot (*Pet. J. Brass.*, 1928, 36, 206).

Reference should be made to the influence which hydrogen-ion concentration may have on " head retention," " colour," and " finings." Too great an acidity produces too rapid an evolution of carbon dioxide, destroying the colloidal protein films which constitute the " head." Windisch and Kolbach (*Woch. Brau.*, 1927, 44, 53, 64) found that the colour was affected by pH ; too high a pH tending to produce a deep colour. The efficiency of the clarification of beer by adding isinglass, which on reacting with any colloidal protein matter, likely to cause " haze," brings about its coagulation, is also dependent upon hydrogen-ion concentration. It is probable that a pH somewhere near the isoelectric point of isinglass is the most satisfactory, for it is known that a beer of too great an acidity refuses to take finings. Accord-

ing to Freundlich and Gordon (*Trans. Faraday Soc.*, 1935, **31**, 915) the isoelectric point of isinglass (prepared from the swimming bladder of the sturgeon) is at *p*H 5·9.
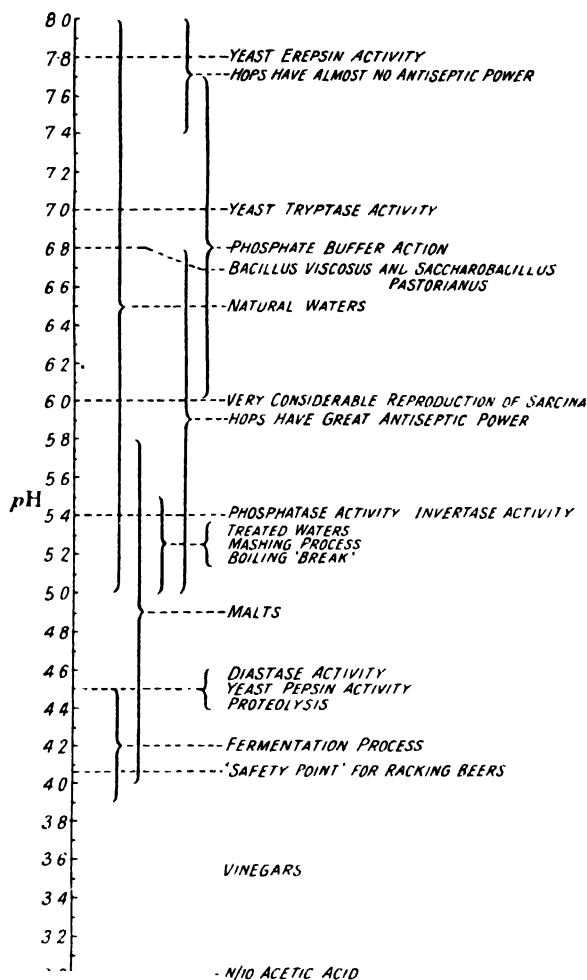
Fig. 175.—Important *p*H values in Brewing.

The chart, Fig. 175, summarises the *p*H's of importance in brewing—it should be noted that the *p*H's at which various enzymes, etc., display their maximum activity have alone been indicated and not the complete *p*H ranges over which they are active.

Volatile Acids in Beer.

Windisch, Kolbach and Schild (*Woch. Brau.*, 1929, **46**, 245, 255) have devised a method by which the volatile acids, *e.g.*, acetic, lactic, may be determined by distillation after the pH of the beer has been set at pH 3 by adding phosphoric acid, tartaric acid and sodium tartrate.

Redox Potentials and rH in Brewing.

The process of fermentation by yeast is governed not only by the pH of the medium, but by the E_h or rH established in the medium. This is determined by the system : cysteine-cystine, originating from the yeast proteins, by the redox systems already in the wort and by the presence of oxygen. Kluyver and Hoogerheide (*Biochem. Zeitsch.*, 1934, **272**, 197) studied yeast fermentations electrometrically under aerobic and anaerobic conditions. Most yeasts under anaerobic conditions at pH 5·4 gave $E_h = + $ 0·08 to $+$ 0·10 volt, but in the presence of oxygen E_h values, ranging from $+$ 0·16 to $+$ 0·31 volt, were observed, depending on the type of yeast employed. Top yeast fermentations, carried out anaerobically, were found by Fromageot and Desnuelle (*Biochem. Zeitsch*, 1935, **279**, 34) to correspond to much lower E_h potentials at pH 6·4, *viz.*, − 0·145 to − 0·185. These observations were made with redox indicators. It should be emphasized here that the indicators themselves are redox systems and may therefore exert their own influence on the systems present in solutions, undergoing test, where the latter are only slightly poised and thus lead to erroneous results.

Fermentation being essentially an oxidation process is associated with a high rH value. Moreover, a high rH is essential for the respiration of yeast. It becomes very slow at rH 15, which at the pH of wort is approximately the condition at which methylene blue is decolourised. Regarding beer, a high rH value, above 21, leads to stability, whereas rH 10 to 18 indicates that the beer has acquired reducing properties and is very susceptible to air-oxidation (Mendlik, *Woch. Brau.*, 1934, **51**, 305). In fact, the rH of beer exposed to the air falls slowly from rH 15·5–17 to rH 10 ; the rate depending on the aeration and the temperature, (de Clerck, *J. Inst. Brew.*, 1934, **40**, 407). The problem of the taste of beer and its keeping qualities are thus seen to be dependent on rH. One way to regulate rH during storage is to employ an atmosphere of carbon dioxide in order to prevent the absorption of oxygen.

The development of *yeast haze* in beer has been studied by

de Clerck (*Bull. Assoc. Anc. Etud., Louvain*, 1934, **34**, 55, 78), who states that if methylene blue is not decolourised in four days, turbidity is likely to follow in due course as the result of slow oxidation. On the other hand, Mendlik points out that haze can develop at low *r*H if a quantity of fermentable sugars is present. From this point of view, it would appear that a low content of fermentable sugars and a low *r*H, maintained by the exclusion of air, are desirable in beer.

Redox indicators which have been advocated for brewing processes are dichlorophenol-indophenol (Hartong, *Woch. Brau.*, 1934, **51**, 409) and thionine, *r*H 15–17; methylene blue, *r*H 13·5–15·5; and indigotin-tetrasulphonate, *r*H 11–13 (Laufer, *Amer. Brewer*, 1936, **69**, 15).

Spirits and Wines.

The importance of hydrogen-ion concentration in the distillery has been the subject of some investigations by Diemair and Sichert (*Biochem. Zeitsch*, 1929, **204**, 414; **210**, 286), Drews (*Z. Spiritusind.*, 1930, **53**, 91), and Dehnicke (*ibid.*, 133). The *p*H of the liquid expressed from raw or steamed potatoes is about 5·9, and that of sweet wort prepared from potatoes and malt is 5·1–5·3, a range which is favourable to the action of diastase. The optimum value for alcoholic fermentation is *p*H 4·5, and consequently to prevent the *p*H becoming much below this value on acidification with either lactic or sulphuric acids it is necessary that the mash shall have a high buffer content. This can be obtained by employing a more concentrated mash and a higher proportion of green malt. The optimum *p*H for the fermentation of maize mashes is 4·58, whilst for Kaffir corn it is 4·52. As maize mashes are not entirely suitable to the activity of yeast, it undergoes decomposition leaving the mashes rich in buffering power through the presence of much protein and protein degradation products. Dehnicke points out that in small distilleries the measurement of *p*H values as a method of controlling fermentation is of little value, as the usual technical methods yield worts of high buffer content. Control of *p*H, however, is of service in the preparation of sulphuric acid yeast.

A method of determining the liquefying power of malt diastase (Józsa and Gore, *Ind. Eng. Chem., Anal. Edn.*, 1930, **2**, 26) involves the liquefying of potato starch paste, buffered at *p*H 4·6, as indicated by viscosimetric measurements.

Mineral acid in wine may be detected by means of *p*H determinations and the buffering powers. Values of *p*H lower than 2·65 are to be attributed to the presence of strong mineral acid

(Morani, *Annali Chim. Appl.*, 1930; **20**, 30). Ordinary wines range from pH 2·65–3·78, though wines of high extract may be even higher.

The bouquet of wines depends on the relative amounts of oxidants and reductants resulting from fermentative processes, which are characterised by the E_h or rH values. According to Geloso (*Ann. Brass. et Dist.*, 1931, **39**, 177, 193, 273, 275) at least two redox systems are involved at 20° in fermentation, *viz.*, one, for which $E_h = -$ 0·115 and another, for which $E_h = -$ 0·160.

Rum.

Rum is distilled from fermented cane sugar products, *e.g.*, blackstrap molasses. For the fermentation various types of yeast are used. In American distilleries, the mash is initially set at pH 5–7, and then lowered to pH 4–4·5 with dilute sulphuric acid. The pH of U.S.A. Rums is about 4·5 and Jamaica Rums vary from pH 3·8 to 4·8. Low pH values generally indicate the presence of sulphuric acid. Whisky varies from pH 4·5 to 6·0.

Vinegar.

Vinegars contain proteins, tannins and pectin and have a pH of 3·2–3·5. Saywell (*Ind. Eng. Chem.*, 1934, **26**, 379) precipitates the tannins with casein at pH 2·7–4·0, which, however, is slightly soluble. By using either citric or tartaric acid in the place of hydrochloric acid its solubility is reduced, and this is especially the case in the presence of 0·1 per cent. of added tannin.

Liebmann and Rosenblatt (*J. Assoc. Off. Agric. Chem.*, 1942, **25**, 163) have reported that the effect of the alcohol in whisky on the quinhydrone electrode is different from that on the glass electrode, and similar observations have been made by Fornachon (*Ind. Eng. Chem., Anal. Edn.*, 1946, **18**, 790) in the case of wines, whose observations are summarised in Table 209.

Technical Fermentation Processes.

n-Butyl alcohol and acetone can be obtained by the anærobic fermentation of sterile molasses or maize syrup with *clostridium saccharo butylacetonicum* at pH 4·0–7·5 at 30° C., which process is followed by ordinary yeast fermentation. (Loughlin, U.S.P., 1,992,921 and 1,996,428).

A similar process involving the use of *clostridium propyl-butylicum* on sugar mashes is that of McCoy, Muller and Legg (B.P. 415,311–2). The pH is regulated at 5·8–6·1 with a slight excess of calcium carbonate and the chief products are *n*-butyl, *iso*propyl and ethyl alcohols, together with some acetone.

TABLE 209

pH VALUES OF WINES

Errors in the pH values calculated from the
Potentials of the Quinhydrone. Electrode (Fornachon)

Wine.	Alcohol content % by vol.	pH indicated by	
		Glass Electrode.	Quinhydrone Electrode.
Sweet Red	19–20	3·45–3·84	3·29–3·69
Dry White	14	3·21	3·18
Dry White (Sherry) . . .	17·5	3·40	3·30
Dry White	10–15	3·22–3·59	3·22–3·56
Dry Red	11·5	3·48, 3·53	3·58, 3·65
White Grape Juice (pasteurised)	0	3·33, 3·42	3·34, 3·41

Employing selected strains of the fungus, *aspergillus niger*, sugar can be converted into oxalic acid and citric acid. By adjustment of the pH to 3·5, the oxalic acid fermentation can be almost entirely suppressed and the citric acid production facilitated. Incidentally, this pH prevents undesirable spore formation and guards against infection by other organisms (Wehmer, *Bull. Soc. chim.*, 1893, **9**, 728 ; *Compt. rend.*, 1893, **117**, 332 ; Currie, *J. Biol. Chem.*, 1917, **31**, 15). Instead of sterilising by heat, it may be effected by acidification with either hydrochloric or sulphuric acid at pH 1·2–2·5 (Fernbach and Yuill, B.P., 266,414,'5/1927 ; U.S.P., 1,691,965,'6/1928). Gluconic acid may be obtained from glucose by fermentation with *aspergillus niger*. Moyer *et al.* (*Ind. Eng. Chem.*, 1937, **29**, 777 ; 1938, **30**, 782) find the maximum rate of conversion is about pH 5, which condition can be controlled by the addition of calcium carbonate. Otherwise, the accumulation of a large quantity of gluconic acid sets up a pH, 2·4–2·6, which exercises a considerable retarding influence on the fermentation.

At the pH of wines (3–6), the rH ranges from 18 to 21 ; old wines being still higher. Wines, which are kept in hermetically sealed bottles, may have rH values below 18. This is necessary in the case of wines which have had to be treated, and their rH thereby lowered, with sulphur dioxide or other reducing agents.

The metal used in wine-containers may influence the rH of the wine, owing to the possibility of introducing redox systems, *e.g.*, $Fe^{\cdots} \rightarrow Fe^{\cdot\cdot}$, through the dissolution of the metal (Casale, *L'Ind. Chimica*, 1934, 303 ; Ferré and Michel, *Ann. Fals.*, 1933, 289 ; Dubaquié, *Rev. Viticulture*, 1933, 2027 ; Flamand, *Bull. Anc. El. Sup. Ferment, Gaud*, 1935, 209).

CHAPTER XL

THE SIGNIFICANCE OF THE HYDROGEN-ION CONCENTRATION OF MILK

Foa (*Compt. rend. Soc. Biol.*, 1905, **57**, 51) was the first to determine the hydrogen-ion concentration of milk by the electrometric method. Interwoven with the hydrogen-ion concentration of milk are many important properties, *viz.*, the degree of freshness and the keeping quality, the natural curdling of milk produced by bacterial action and the rate at which it takes place, the presence of blood serum, and the general composition of the milk.

pH and Titratable Acidity.

The acidity of milk is usually regarded as being either " natural " or " developed," the former being the acidity immediately after drawing from the cow, and the latter being that developed by bacterial action on standing. It may be considered in terms of titratable acidity or hydrogen-ion concentration. Titratable acidity is found by titration to phenolphthalein with sodium hydroxide and calculated in terms of lactic acid. Actually the acidity is produced by a number of factors. Thus Rice and Markley (*J. Dairy Sci.*, 1924, **7**, 468) found that the titratable acidity of freshly drawn milk, calculated as lactic acid, was from 0·01 to 0·02 per cent. due to the carbon dioxide in the milk, 0·01 per cent. to acid citrates, 0·05 to 0·08 per cent. to casein, less than 0·01 per cent. to albumin, and the remainder to phosphates. The natural acidity of milk varies between wide limits, and in extreme cases the milk drawn from individual cows may vary from 0·086 to 0·275 per cent. Usually, it varies from about 0·100 to 0·175 per cent., the average value being around 0·136 per cent. High titratable acidity of fresh milk samples may be taken as an indication of high buffer action. According to Van Slyke and Baker (*J. Biol. Chem.*, 1919, **40**, 342) the normal pH range of fresh milk is 6·5 to 6·65. It appears that, in a general way, a high fat content, a high content of solids-not-fat, and high hydrogen-ion concentration of fresh milk are related. They also observed that with diminishing hydrogen-ion concentration, there is a general tendency for the carbon dioxide to increase, whilst the titratable acidity decreases. The decrease is not so marked between pH 6·50

and 6·65, as it is above pH 6·65. The composition of milk varies with its pH value while fresh, as may be seen from the data given in Table 210, which are a selection of those given in Van Slyke and Baker's paper.

TABLE 210

pH OF FRESH MILK AND ITS PERCENTAGE COMPOSITION

pH.	Fat.	Casein.	Other Proteins.	Sugar.	Ash.	Chlorine.	S.G.
6·53	4·50	2·55	0·66	4·60	0·70	0·09	1·029
6·58	5·40	2·75	0·85	5·10	0·72	0·10	1·032
6·70	3·60	2·50	0·71	4·40	0·86	0·13	1·030
6·85	5·40	2·20	0·80	4·50	0·81	0·14	1·030
6·95	2·40	2·05	1·09	3·80	0·83	0·16	1·030
6·98	2·80	1·79	1·01	4·00	0·81	0·15	1·027
7·15	2·10	1·71	1·43	3·00	0·89	0·21	1·026

As these results show, there is a tendency for the specific gravity of milk to become smaller with increasing pH. This diminution is accompanied by a reduction in the percentage amounts of total solids, fat, solids-not-fat, casein, and sugar ; and an increase in lactalbumin and proteins other than casein, and in the inorganic matter (ash) and also in the chlorine. An increase was, moreover, found to occur in the carbon dioxide content. The fact that an increased pH of fresh milk is associated with changes in the composition of the milk, including a greater carbon dioxide content, led Van Slyke and Baker to suspect that these variations were caused either by the presence of blood serum or lymph, or to an easier diffusion of the contents of blood into the milk. Despite the fact that the milk had been drawn from udders which appeared to be in a healthy condition, these variations are such as would be introduced by blood serum. Thus the pH of normal fresh milk lies between 6·5 and 6·6, that of blood serum is 7·6, and whereas the carbon dioxide content of normal milk is about 10 per cent. by volume, the content of the latter is about 65 per cent. The increase in the number of leucocytes found in milk of pH higher than 7 seemed to add support to this view, so also did the fact that fibrin was found in milks of pH 6·9. to 7·2. Conclusive evidence was, however, not forthcoming, for glucose which is a constituent of blood serum could not be detected in the milks in question. Blood serum has been found by many workers in milk taken from diseased udders, in which case it might have found its way either by direct filtration into the lumen of the alveoli without undergoing transformation by the gland cells, or through lesions caused by bacterial activity. Baker and

M*

Breed (*J. Biol. Chem.*, 1920, **43**, 221) obtained similar results in that they found that milk of high *p*H usually contained an increased number of leucocytes and epithelial cells, and also that the percentage number of samples containing streptococci increased with the *p*H.

Bromocresol purple has been used by Baker and Van Slyke (*J. Biol. Chem.*, 1919, **40**, 357, 373) for the routine examination of milk. When 1 drop of a saturated aqueous solution is added to 3 c.c. of milk, normal fresh milk assumes a greyish-blue colour. More alkaline milks, such as those drawn from diseased udders, or those which have been watered or skimmed, or those to which salts having an alkaline reaction have been added, produce a darker colour and should consequently arouse suspicion. More acid milks, due either to developed acidity, or to having been heated above the usual temperature of pasteurisation, give rise to lighter colours. By detailed investigation of suspected samples of commercial milk they were able to detect watered milk, and milk containing an excessive number of leucocytes. They also studied the rate of development of acid due to the bacteria contained in the milk by following the colour changes of the indicator after incubation in sterilised vessels for different periods of time at a given temperature. To some extent, such a test gives an idea of the keeping quality, though other factors which should be considered are (*a*) the coagulation of the casein, (*b*) the development of abnormal odour and taste, (*c*) production of gas, etc. Larger numbers of bacteria were contained in the more acid samples than in the other samples. Similar observations have been made by Cooledge (Michigan Agr. Exp. Station, *Tech. Bull.*, 52, 1921) using bromo-thymol blue. He has also devised a test of the keeping quality by incubating at 37° C. 0·1 c.c. of milk in a tube of broth containing this indicator and making colorimetric *p*H measurements every hour for eight hours.

Bacterial fermentation gives rise to that additional acidity known as " developed acidity." This form of acidity is of great importance in the manufacture of evaporated milk, for it lowers the coagulation temperature, and as a consequence, may lead to serious loss on the milk so treated. As the coagulation temperature of milk is above 100° C., it is necessary to employ increased pressures of 2 to 4 atmospheres to prevent boiling. It is often found that milk with high natural acidity will not coagulate until a higher temperature is attained than that required for the coagulation of less acid milk. On the other hand, a slight increase in the developed acidity above the natural acidity of the same milk will cause the milk to settle out at a lower temperature.

Table 211, which presents the data of Rogers, Deysher, and Evans (*J. Dairy Sci.*, 1921, **4**, 4), gives an example of the development of titratable acidity, with lowering of *p*H of the raw milk, its effect on the *p*H of the evaporated milk and its coagulation temperature. It also gives the bacterial counts. (*See* also Holm, Deysher, and Evans, *J. Dairy Sci.*, 1923, **6**, 6, who obtained analogous results.)

TABLE 211

DEVELOPMENT OF ACIDITY

Age. Hours.	Number of Bacteria in 1 c.c of Raw Milk		Titratable Acidity as per Cent. Lactic Acid.	*p*H of Raw Milk.	*p*H of Evaporated Milk.	Temperature of Coagulation ° C.
	Total Millions.	Lactic Millions.				
0	1·14	0·79	0·170	6·57	6·33	119
3	47·5	30·5	0·175	6·51	6·27	113
4½	96·0	53·5	0·207	6·43	6·21	11c

A word here on the manufacture of evaporated and condensed milks will suffice to show the importance of the coagulation temperature, and the risk entailed in using milk with a too highly developed acidity. The milk is usually subjected to a preheating treatment extending from 1 to 20 minutes at a temperature between 82 and 99° C., and then evaporated in vacuo between 54° and 71° C. until the desired consistency is attained. The milk is run into cans and sealed. Sterilisation of the canned milk is effected by heating to between 107° and 116° C., when every effort is made to prevent separation of the casein by efficient agitation. If coagulation has occurred, through the use of sour milk, this may often not be discovered until the can is opened by the user.

The existence of too great an acid-content in condensed milk may have a deleterious effect, on account of the production of lumps of separated casein. Such an acidity may arise from a yeast which causes the fermentation of the cane sugar, or from acid-forming bacteria, or from the use in canning of an acid flux, *e.g.*, hydrochloric acid and zinc chloride. Fluxes likely to contaminate the milk, and especially those which may influence the *p*H of the milk should be avoided. Rosin dissolved in alcohol or in petrol is to be preferred.

Cause of Acidity.

In order to trace the cause of the acidity of milk, we must pay some attention to the composition of milk. The composition

of a typical commercial sample of cow's milk is given in Table 212.

TABLE 212
COMPOSITION OF MILK (TYPICAL)

Bases.		Acids.		Proteins
KOH .	0·038 N	H_3PO_4 .	0·063 N	Casein . 28·0 gm. per litre
NaOH .	0·023 N	Citric. .	0·029 N	Albumin . 7·2 ,, ,,
Ca(OH)₂ .	0·064 N	HCl .	0·028 N	Other
Mg(OH)₂ .	0·016 N	H_2SO_4 .	0·003 N	Protein 0·2 ,, ,,
Fat .				. 50 gm. per litre.
Sugar				47 ,, ,, ,,

Lactic acid is not present in freshly drawn milk. It is the acid which is responsible for the developed acidity. Neither the fat nor the sugar has an effect on the hydrogen-ion concentration of milk. Hence the pH of fresh milk is determined by the reactions which take place between the several bases and the acids and amphoteric bodies (the proteins), which in a system like that of milk behave as acids at about pH 6·5. It is evident that at pH 6·5 the equilibria which must be involved are—

$$\text{(i) BOH + Protein} \rightleftharpoons \text{B Proteinate} + H_2O,$$
$$\text{(ii) BOH + } BH_2PO_4 \rightleftharpoons B_2HPO_4 + H_2O,$$
and $$\text{(iii) BOH + } BH_2\text{Citrate} \rightleftharpoons B_2\text{HCitrate} + H_2O,$$
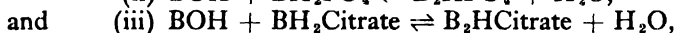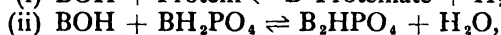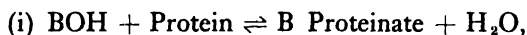
where B represents the equivalent of any of the strong bases given in Table 212. If we consider the data given in the table, we find that the total concentration of bases is 0·077 N, whilst the total concentration of acids which form either neutral salts or acid salts below pH 6·5, e.g., NaH_2PO_4 and NaH_2Citrate, is 0·061 N. Hence a concentration of 0·016 N of the bases will be free to form either of the secondary salts, Na_2HPO_4 and Na_2HCitrate, and to react with the casein and other proteins. As the casein is in a preponderating amount it appears that in milk much of the excess base will combine with it. Harris (*Proc. Roy. Soc.*, 1924, **97**, B, 372) has pointed out that if separate pH-acid combination curves for each of these constituents be plotted, making the abscissæ proportional to the percentage amounts present, the resultant curve obtained by summation gives a pH-acid combination curve for the whole milk, which will be found to agree excellently with the experimentally determined curve. In general, the ash in milk bears a direct relationship to the protein in the ratio of 2 : 9, e.g., Richmond (*Dairy Chemistry*, p. 152, 2nd ed., London, 1914) gives protein 37·8 per cent., and ash 8·3 per cent.,

of the solids-not-fat, and•of this ash the phosphate and citrate
.contents are approximately constant. Furthermore, the lactal-
bumin bears a small, but definite, ratio to the casein content.
On these grounds, Harris argues "‚that in moderately acid solu-
tions the buffer value of normal cow's milk is directly proportional
to the amount of protein present (as also, therefore, to the phos-
phate, citrate, etc.)." A pH curve of 100 c.c. of a representative
sample of milk is given in Fig. 176, which is reproduced from a
paper by Clark (*J. Dairy Sci.*, 1927, **10**, 199).

Estimation of Protein in Milk.

Based on the above statement, Harris has devised a method by
which he claims that the protein in milk can be estimated within
o·1 per cent. It is only necessary to run from a burette successive
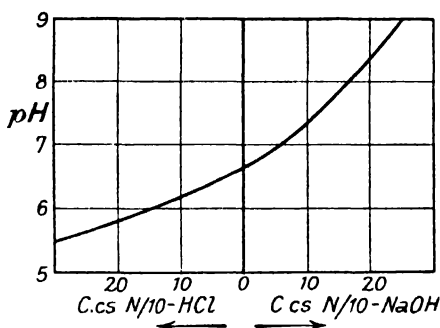
FIG. 176.—pH Curve of 100 c.c. of Milk.

small amounts of decinormal hydrochloric acid to a measured
volume of milk and to determine the pH after each of three
or four additions. These should be sufficient to construct a
pH-acid curve, and as the curve is practically rectilinear, it is
possible to interpolate the amount of N/10-HCl to be added to
take the pH of the milk from one given value to another. Such
an amount of acid will be proportional to the protein content.
By choosing 10 c.c. of milk as the volume to be titrated and the
pH range, 6·65 to 5·2, the amount of N/10-HCl may be taken as
numerically equal to the percentage of the protein in the milk.
Harris adds that the readings should be taken only within the
range, pH 6·7 to 4, the reason for which will be apparent from
Fig. 176. Clark finds the buffer capacity, *i.e.*,

$$\frac{d\mathrm{B}}{dp\mathrm{H}} = \frac{\text{Equivs. acid or alkali added to 1 litre}}{\text{Change in } p\mathrm{H}},$$

of the milk at pH 6·0 to be 0·0242 and 0·0186 at pH 6·6. It is interesting to compare these values with that of blood. As is well-known, human blood is well buffered and at pH 7·4 $\dfrac{dB}{dp\text{H}} = 0·0228$. The buffering of milk has been studied recently by Buchanan and Peterson (*J. Dairy Sci.*, 1927, **10**, 224).

It happens that if different samples of milk had widely differing buffer capacities, a highly buffered milk would resist the action of the lactic acid, developed by means of bacteria, as regards its hydrogen-ion concentration to a greater extent than a poorly buffered sample. In the former case, considerably more lactic acid would be required to cause the milk to coagulate than in the latter. For milk to curdle the hydrogen-ion concentration is of utmost importance ; so also is it in regard to the rate at which curdling takes place. The hydrogen-ion concentration should be adjusted to the iso-electric point of casein, *viz.*, pH 4·7. Michaelis and Mendelssohn (*Biochem. Zeitsch.*, 1915, **58**, 315) found that the optimum concentration of hydrogen ions required to precipitate casein by acids in pure solutions or in milk is $2·5 \times 10^{-5}$, and Allemann (*Biochem. Zeitsch.*, 1912, **45**, 346) obtained $1·3 \times 10^{-5}$ as the minimum concentration. Van Slyke and Baker (New York Agric. Exp. Station, Geneva, *Tech. Bull.*, **65**, 1918) coagulate the pure casein from milk at pH 4·64 to 4·78 by carefully introducing hydrochloric and lactic acids into the body of the milk and then centrifuging. The correct acidity is adjusted with bromocresol purple. Waterman (*J. Assoc. Off. Agr. Chem.*, 1927, **10**, 259) uses for the precipitation of the casein a buffer mixture which controls the pH of precipitation within a range of about 0·04 for fresh milk samples, and precipitation is effected at a pH very near to the isoelectric point of casein.

As a rule, fresh milk having a high hydrogen-ion concentration has also a high titratable acidity due to the presence of a high acid phosphate and, maybe citrate, content. Such milk, despite its acidity, is of greater nutritive value than milk low in acid. The casein content of the more acid milk is higher. It is also found, as might be expected, that fresh milk of low pH undergoes a smaller variation in hydrogen-ion concentration on the addition of either acid or alkali. High acid milks are of importance commercially for this reason, for on storing they take longer time to reach the point of coagulation than low acid milk. The carbon dioxide content of milk remains fairly constant, though there is a tendency for milk of high pH to contain greater amounts.

We have seen on page 121 that calcium phosphate begins to precipitate under conditions of equilibrium at about pH 5·5,

whilst at higher *p*H values, it becomes increasingly insoluble. It is probably the complexity and colloidal nature of the milk system which prevent the precipitation of calcium phosphate from ordinary milk. It is, incidentally, extremely probable that both the calcium and the phosphate are much more readily assimilated from a highly acid fresh milk than from a less acid milk—a point which may have bearing on the prevention of rickets (*cf.* Clark, *J. Dairy Sci.*, 1927, **10**, 199).

Colorimetric Determination of the *p*H of Milk.

The adsorption of the indicator by the casein in milk presents difficulty in the measurement of its hydrogen-ion concentration. Hence, various methods have been adopted in which the casein is eliminated by dialysis, or its effect minimised by dilution (*cf.* Schultz and Chandler, *J. Biol. Chem.*, 1921, **46**, 129 ; Schultz, Marx, and Beaver, *J. Dairy Sci.*, 1921, **4**, 1 ; Kramer and Greene, *J. Biol. Chem.*, 1921, **46**, 42 ; Brown, *J. Physiol.*, 1920–1, **54**, 167).

The dilution method has been carefully investigated by Sharp and McInerney (*J. Biol. Chem.*, 1926, **70**, 742). They dilute 1 part of the milk product with 19 parts of distilled water, and then perform the colorimetric determination of the *p*H value with the comparator as described on page 415, Vol. I. The values so found are too high. Table 212 gives the true *p*H values of both the undiluted milk and the undiluted whey corresponding to the observed values on the diluted samples. The values given in the second column also refer to whole and skim milk and to heated milk. They may be used for evaporated milk, if it first be diluted to the consistency of whole milk, and further diluted as stated above. The *p*H values of undiluted whey do not apply if a part of the casein only has been precipitated, and moreover, if satisfactory values for whey are to be obtained the determinations must be made immediately after the curd has been separated. The amount of indicator recommended is 5 drops of 0·1 per cent. solution to each 10 c.c. of solution.

Concerning the *p*H of cream, Sharp and McInerney state that fresh cream is supposed to have the same hydrogen-ion concentration as the skim milk which may be centrifuged from it. Provided the cream has not developed acidity, in which case the skim milk will contain products intermediate between curds and whey, the foregoing dilution method can be adopted and the relationships given in columns I. and II. of Table 212 will hold good. For sweetened condensed milk, they dilute the milk with distilled water back to the average solids-not-fat composition of the uncondensed milk, and then to 20 volumes before determining

TABLE 213 *

RELATION BETWEEN pH OF DILUTED MILK AND OF ORIGINAL MILK

Observed pH Diluted Product.	pH Undiluted Milk.	pH Undiluted Whey.	Indicator.
7·4	6·86	—	
7·3	6·76	—	
7·2	6·66	6·94	
7·1	6·56	6·84	Phenol Red
7·0	6·46	6·74	
6·9	6·36	6·64	
6·8	6·26	6·54	
6·7	6·16	6·44	
6·6	6·06	6·34	
6·5	5·96	6·24	Bromo-cresol purple
6·4	5·86	6·15	
6·3	5·76	6·05	
6·2	5·66	5·96	
6·1	5·57	5·87	
6·0	5·48	5·77	
5·9	5·40	5·68	
5·8	5·32	5·58	
5·7	5·24	5·48	Chloro-phenol Red
5·6	5·17	5·38	
5·5	5·11	5·28	
5·4	5·05	5·18	
5·3	4·99	5·08	
5·2	4·92	4·98	
5·1	4·86	4·88	
5·0	4·78	4·78	
4·9	4·71	4·68	
4·8	4·62	4·58	Bromo-cresol Green
4·7	4·53	4·48	
4·6	4·44	4·38	
4·5	4·34	4·28	
4·4	4·25	4·18	
4·3	4·15	4·08	Bromo-phenol Blue
4·2 (?)	4·05	3·98	
4·1 (?)	3·94	3·88	
4·0 (?)	3·84	3·78	

the pH. The values given in Table 213 are not applicable. For a normal product so treated, 0·85 pH is subtracted from the observed value in order to arrive at the hydrogen-ion concentration of the reconstituted milk. The pH of the sweetened condensed milk is approximately 0·30 pH less than the latter value.

Relation between Titratable Acidity and pH.

The work of Sharp and McInerney (*J. Biol. Chem.*, 1927, **75**, 177) has shown that there exists between the titratable acidity of

fresh milk, if it be greater than 0·1 per cent., and *p*H a relation by which the *p*H value can be ascertained with an average error of ± 0·06 *p*H. This relation is expressed by the heavy curve in Fig. 177. The thin lined curves show the development of acidity by the souring of samples of milk, whose acidities, when fresh, are
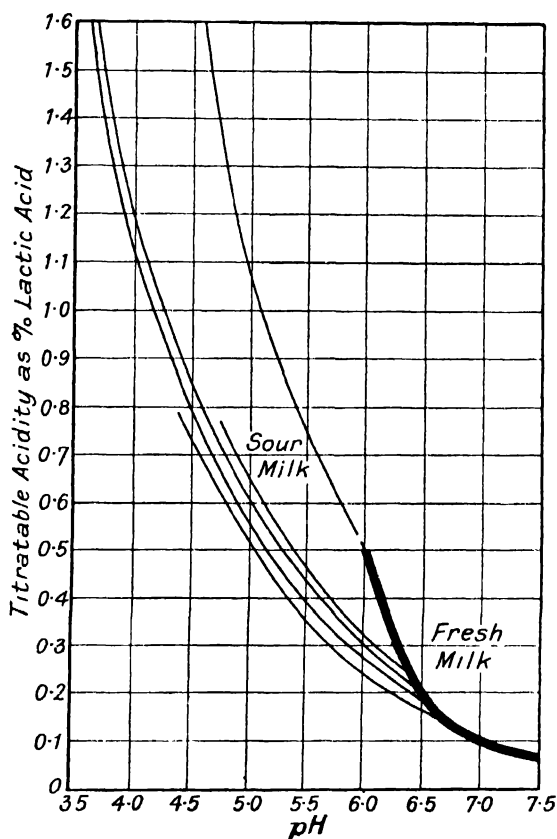
Fig. 177.—Relation between the *p*H of Fresh and Sour Milk.

represented by the points of intersection of these curves and the heavy lined curve. It will be seen therefrom that quite a different relationship exists between the titratable acidity of sour milk and the *p*H readings. From this, it follows that a knowledge of both the titratable acidity and the *p*H value of a milk may be of great value in ascertaining the condition of the acidity of the milk, whether it be natural or developed. Titratable acidity, by itself,

is of little use in this respect.   In order to make these investigations as complete as possible Sharp and McInerney studied, as shown by Fig. 177, samples of fresh milk which ranged in titratable acidity from 0·50 per cent. to 0·05 per cent. as lactic acid and from pH 6·0 to pH 7·73.   The milks corresponding to the extreme pH values were abnormal.   Thus, those of abnormally high titratable acidity and high hydrogen-ion concentration were all samples of colostrum milk or milk drawn in the early days of lactation, though it should be mentioned that samples of the latter were not always of abnormal acidity.   It is interesting to note that they found the milks at the other extreme, *viz.*, high pH, often contained large numbers of leucocytes, which in many cases were traced either to diseased udders, or to gargety milk, or to cows which had not been milked for some time.   In view of these abnormalities, it is somewhat surprising that the general relationship shown by Fig. 177 should exist.   Grimmer and Arlart (*Milchw. Forsch.*, 1930, **9**, 100) has also devised a method of calculating the pH of milk from its titratable acidity, based on the variation in pH with the square of the acidity, represented on the Soxhlet-Henkel Scale.

Mayoroff (*Z. Unters. Lebens.*, 1935, **69**, 301) points out that very often changes in pH occur between milking and the time of testing.   Thus in 3 to 5 hours an initial increase in pH occurs, which he attributes to some decomposition of the albumin, which may necessarily not influence the titratable acidity.   Thus the separation of lysine, arginine and histidine, which constitute about 15 per cent. of casem, would have no effect on the acidity, although these amino-acids would tend to raise the pH.   It is, however, purely conjectural whether any amino-acids do actually separate from casein under the conditions existing in freshly drawn milk.

A difficulty that sometimes arises in the washing of milk churns with alkaline detergents is the formation of " milk stone " on the surface of the churns and this acts as a nutrient medium for bacteria.   Parker (*Milk Plant Mthly*, 1941, **9**, 49) states that if a solution of either gluconic or lævulic acid is injected with steam into the churns before washing with an alkaline detergent a pH of 6·0 to 6·5 will then be set up and so ensure satisfactory cleaning.

According to Baetslé (*Le Lait*, 1937, **17**, 141) milk, which has been neutralised, may be detected by adding 30 c.c. of methyl alcohol to 20 c.c. of milk and after stirring three times at intervals, whereas the protein from pure milk coagulates in the form of large masses and leaves a clear serum of pH 6·3–6·5,

neutralised milk does not coagulate completely, but leaves a turbid serum, the *p*H of which is always higher than 6·5.

Cows' milk, on account of its appreciable buffer action and high *p*H, is somewhat difficult to digest by infants. It may be improved by adjusting the *p*H value to approximately that of human milk, *viz.*, about *p*H 5·5. Hess and Matner (*J. Amer. Med. Assoc.*, **82**, 1604) have found that lemon juice or orange juice can be added directly to cows' milk without curdling, and that by mixing approximately 21 c.c. of lemon juice with a quart of milk the *p*H value fell from 6·64 to 5·54. They state that the infants who received milk so treated, thrived. Either lactic or hydrochloric acids may be used, but lemon juice is to be preferred in that it compensates for the deficiency in cows' milk of anti-scorbutic vitamin. The addition of egg yolk to the treated milk is without any marked change on its *p*H value. Another method of preparing milk for infant feeding consists of heating to 62·5° C. for half an hour, homogenising at 2800 lb. pressure, cooling to 42·5°, inoculating with a lactobacillus culture and maintaining at that temperature until the *p*H reaches 3·5 (Rogers, U.S.P. 1,722,710/1929).

Milk Shakes.

A difficulty in the preparation of " milk-shakes " arises from the fact that the fruit juices are appreciably acidic and they may therefore lead to the coagulation of the casein in the milk. This occurs when the isoelectric point of casein, *p*H 4·6, is reached. Acidification to *p*H 5·0–5·4 causes an appreciable increase in viscosity and on standing partial separation occurs. At *p*H 5 separation does not occur for at least 5 minutes.

Davies (*J. Soc. Chem. Ind.*, 1937, **56**, 10T) has measured the *p*H of fruit juices, synthetic flavourings and 1·75 per cent. citric acid, together with their titratable acidities and " buffer-indexes." Some of his data are recorded in Table 214.

Citric acid is the chief acid in fruit juices and is present in concentrations ranging from 0·02–0·13 M. It causes buffering between *p*H 3 and 7·5.

The values of *k* in Table 214 are defined by the equation : $pH = 6\cdot60 - k \log_{10}n$, where *n* is the number of cubic centimetres of fruit juice which can be added to 50 c.c. of milk to bring it to any desired *p*H. For the more acid fruit juices, $k = 8B + 1\cdot2$, and therefore $pH = 6\cdot6 + (8B + 1\cdot2) \log_{10}n$. Neither of these equations hold for synthetic and low-acid natural juices owing possibly to the comparatively greater effect and different behaviour of buffers other than the citric acid—citrate system.

Butter.

The putrefaction of butter is very often associated with the presence of the organism, *achromobacter putrefaciens*, which readily tolerates a pH between 5·2 and 7·8. Its development is inhibited at pH 4·2 (Claydon, *Iowa State Coll. J. Sci.*, 1939, **14**, 17).

TABLE 214

INITIAL pH TITRATABLE ACIDITIES AND BUFFER INDEXES OF SOME NATURAL AND SYNTHETIC FRUIT JUICES

Juice.	pH.	Titratable Acidity (A). C.c. N-NaOH per 100 c.c. Juice.		Buffer Index (B).	A B	k.
		Electro-metric.	Phenol-phthalein.			
Natural :						
Strawberry . . .	3·2	5·4	5·4	0·015	360	0·61
Blackcurrant (*a*) . .	3·5	12·0	12·1	0·035	347	1·49
,, (*b*) . .	3·5	22·5	21·9	0·063	331	1·73
Raspberry . . .	2·9	15·5	15·6	0·035	441	1·42
Loganberry . . .	2·5	49·0	48·5	0·117	415	2·17
Synthetic :						
Blackcurrant . .	2·8	6·3	—	0·015	420	0·81
Raspberry . . .	2·8	6·3	—	0·015	420	0·81
Citric acid, 1·75 per cent	2·0	25·0	25·0	0·058	431	1·71

On the other hand, an acid serum (*i.e.*, the liquid squeezed out of the butter) having a pH less than 6·4 gives a low storage quality, due to bacterial action on the butter fat. Deterioration is more marked in the case of butters which are more highly flavoured, even though they may have the same pH (Gilmour and Arup, *Ice and Cold Storage*, 1935, **38**, 120).

On storage, butter may develop a fishy flavour on its surface due to deterioration accompanied by the development of a low pH. To guard against this White (*Sci. Agric.*, 1942, **23**, 41) recommends that butter which has to be stored should have an optimum pH value of 6·7–6·9.

The mode of estimating the titratable acidity of butter, by titrating either aqueous, alcohol-ether, or alcohol extracts to phenolphthalein, is not altogether satisfactory owing to the indefinite end-points which are caused by saponification of fat. Nissen (*Ind. Eng. Chem., Anal. Edn.*, 1931, **3**, 374) suggests the electrometric titration of the lower layer obtained after separating the curd-serum layer from the fat by heating the butter for 1 hour at 71–77° C. The pH of the sera ranged from 4·80 to 7·69. Parks and Barnes (*ibid.*, 1935, **7**, 71) have found the glass, hydro-

gen and quinhydrone electrodes to be applicable to milk, butter-milk, cream, butter serum and ice-cream. Using platinum in con-junction with quinhydrone a decided drift in potential was ob-served in the case of butter serum and ice-cream, but this could be avoided by using gold electrodes. Owing to complex forma-tion with the hydroxy acids present antimony electrodes are unserviceable.

* * * * *

Another case in which the adjustment of the hydrogen-ion concentration has been put to practical use is the separation of milk-fat from sour cream (Stevenson, U.S.P. 1,397,664/1922). Hydrochloric acid is added to the diluted cream until *p*H 3·0 is attained, at which value the precipitated casein will have redis-solved, so that the milk-fat may be separated centrifugally.

Cheese.

Fear and Murphy (U.S.P., 2,326,132) recommend that the *p*H of all milk to be used for cheese-making should be adjusted to *p*H 6·6–7·4 by the addition of either calcium or magnesium oxide in order to give greater uniformity in processing and in flavour, whilst Belousov (*Molochnaya Prom.*, 1950, **11**, (6), 9 ; (7), 7) emphasises that a low *p*H at any stage in the manufacture of cheese will result in defective quality. He states that the optimum *p*H of cheese after pressing lies between 5·3 and 5·9 and that it is within these limits are the cheeses of superior quality, taste and consistency.

Hydrogen-ion concentration control in the making of Swiss cheese has been advocated by Sammis and Santschi (*J. Dairy Sci.*, 1924, **7**, 83) and by Watson (*Ind. Eng. Chem.*, 1927, **19**, 1272). The former add 1 drop of 0·01 per cent. solution of bromocresol purple to 1 c.c. of well-mixed whey, and when the acidity has developed to the extent required just to turn the indicator yellow, they proceed with the final step in the process. Watson uses the quinhydrone electrode.

Casein.

Three methods are used for the precipitation of casein from skimmed milk : (1) by the action of rennet at 96° F., (2) by warming to about 100° F. and allowing souring to take place spon-taneously, and (3) by adding either sulphuric or hydrochloric or acetic acid. To obtain the best results either method requires careful control. To obtain a uniform casein by the last method Nabenhauer (*Ind. Eng. Chem.*, 1930, **22**, 54) states that only enough acid should be added gradually and intimately mixed

until pH 4·6–4·8 is reached at 95° F. At this stage a clean separation occurs, but if too much acid be added the casein will begin to dissolve, thereby softening it and making handling difficult. Caseins may be classified, according to Mummery and Bishop (*Analyst*, 1930, **55**, 367), in terms of the pH values of borax solutions in which specified amounts have been dissolved. The higher the pH value, the smaller the amount of mineral acid contained in the casein, and therefore the better is its quality.

The pH of aqueous extracts of casein is directly connected with the extractable (free) acidity and not so much with the total acidity. This will be clear from Table 215 which gives some data obtained by Snyder and Hansen (*Ind. Eng. Chem., Anal. Edn.*, 1933, **5**, 407).

TABLE 215

pH, FREE ACIDITY AND TOTAL ACIDITY OF CASEIN SAMPLES

| Sample. | pH. | Acidity. | |
		Free.	Total.
Pure	5·64	1·65	9·75
Commercial	4·21	7·15	14·10
,, ...	4·11	9·55	13·60
,, ...	3·81	10·95	14·01
,, ...	3·90	12·85	14·75

The free acidity refers to the titres (c.c.) of 0·1 N-NaOH required to neutralise to phenolphthalein a 10-gram casein extract in 100 c.c. water (five hours being allowed for the extraction), whereas the total acidity is the titre of 0·1 N-NaOH to phenolphthalein obtained indirectly by dissolving 10 grams of casein in 0·1 N-NaOH and back-titrating with 0·1 N-H_2SO_4 to phenolphthalein.

Lactose is manufactured from whey in a manner similar to that used for ordinary sugar refining, with the same precautions as to pH values (see, however, Troy and Sharp, *J. Dairy Sci.*, 1930, **13**, 140). The extraction of lactose from whey by means of alcohol can be facilitated by adjusting the pH to 2·75. This prevents the contamination by nitrogenous and insoluble materials (Leviton and Leighton, *Ind. Eng. Chem.*, 1938, **30**, 1305).

The germicidal properties of alkaline washing solutions used in cleaning milk bottles have been investigated by Myers (*J. Agric. Res.*, 1929, **38**, 521) with special reference to pH and buffer index. Except in the case of solutions containing chlorine, germicidal action increased at the higher pH.

Redox Potential of Milk.

A test used to ascertain whether milk is fresh or has been heated is that due to Schardinger (*Z. Nahr. Genussm.*, 1902, **5**, 1113), which is based on the assumption that the enzymic activity
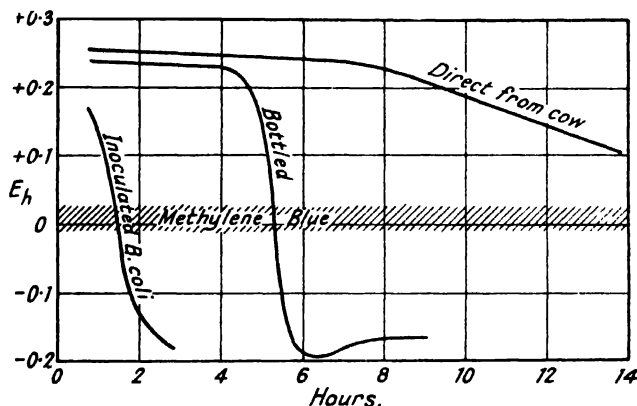
Fig. 177A.—" Redox " Potentials of Milk and the Use of Methylene Blue.

of fresh milk is destroyed by heating. The test consists of adding 5 c.c. of a 1 per cent. formaldehyde solution and a little methylene blue to 100 c.c. of milk and incubating at 37°. Milk, which has been heated, decolorises methylene blue in much greater time than fresh milk. It would appear, therefore, that the redox potential, E_h, of heated milk falls less readily than that of fresh milk. This has been shown to be the case by Clark (*U.S. Hygienic Lab.*, *Bull.* 151, 1928) by the electrometric method.

Fig. 177A illustrates the changes with time at 30° in the redox potential of milk (*a*) as drawn directly from the cow, (*b*) which had been subjected to the ordinary bottling processes, and (*c*) which had been bottled and heavily inoculated with *B. coli*. The E_h at which methylene blue is decolorised, as shown in Table 159, depends on the *p*H of the medium. An approximate value of the E_h at which methylene blue is decolorised is shown in Fig. 177A ; the precise value, however, depends on the *p*H acquired by the milk at the point at which the redox indicator is actually decolorised.

It should be emphasised that Fig. 177A refers to the redox potentials set up in milk alone, *i.e.*, to which no formaldehyde was added. Clark has shown that the presence of formaldehyde considerably lessens the time required for the milk to acquire the redox potential necessary to decolorise methylene blue at 37° C. He has also indicated that the time required depends on the *p*H of the milk.

CHAPTER XLI

THE HYDROGEN-ION CONCENTRATION OF HENS' EGGS

DURING recent years the cause of the deterioration of eggs has received some attention from the standpoint of the variations of the pH of egg-white and yolk that take place on keeping and during incubation. Thus Baird and Prentice (*Analyst*, 1930, **55,** 20) have described some researches undertaken to find whether the hydrogen-ion concentration of egg-white or egg-yolk could be used as a means of determining the age of an egg in cases of legal dispute. They found that the pH of freshly laid eggs is 7·6, and that of yolk is 6·0. According to the Food Investigation Report, 1934, page 50, the pH values are 7·97 and 6·2 respectively. During the first seven days a rapid increase in the pH of the white to a constant figure of approximately 9 occurs ; the yolk, however, undergoes only a very slight increase from pH 6. In consequence, they concluded that hydrogen-ion concentration was of no value in determining the age of commercial eggs. The work by Sharp and Powell (*Ind. Eng. Chem.*, 1931, **23,** 196) clearly shows that pH is an important factor in controlling the rate of deterioration of eggs, and their work brings to light the conditions that must be satisfied in preservation processes. The changes that occur in the pH value of egg-white on ageing have been traced to the loss of carbon dioxide. Scholl (*Arch. Hyg.*, 1893, **17,** 535) showed that fresh egg-white contained a considerable amount of carbon dioxide and concluded that it is largely present in the form of sodium bicarbonate which tends to decompose. It is very probable, as was suggested by Aggazzotti (*Arch. Entwicklungsmech. Organ.*, 1914, **40,** 65), that before laying, the liquid of the egg has the same partial pressure of carbon dioxide as that in the tissues of the hen, and that on laying some of this carbon dioxide passes into the ·air cell. On keeping, carbon dioxide escapes from the egg-white with a consequent rise in pH, which Sharp and Powell find may rise as high as pH 9·7. Healy and Peter (*Amer. J. Physiology*, 1925, **74,** 363) give pH 9·5 as the reaction after eight days and 9·7 after a month.

The isoelectric point of egg-albumin is at pH 4·7 and the farther a protein is from its isoelectric point the more rapid will

be its rate of decomposition. In the case of egg-white, this is
apparent by the white becoming watery, which in turn gives rise
to a weakening of the yolk. For this reason, it is important
that the *p*H of egg-white should be kept as near as possible to its
original value, and this can be done by preventing the loss of
carbon dioxide, or, in other words, keeping the buffer system of
egg-white intact. Fig. 178 shows some of the results of Sharp
and Powell. The curves at the top of the diagram give the
variations in *p*H value of egg-white when the eggs were stored
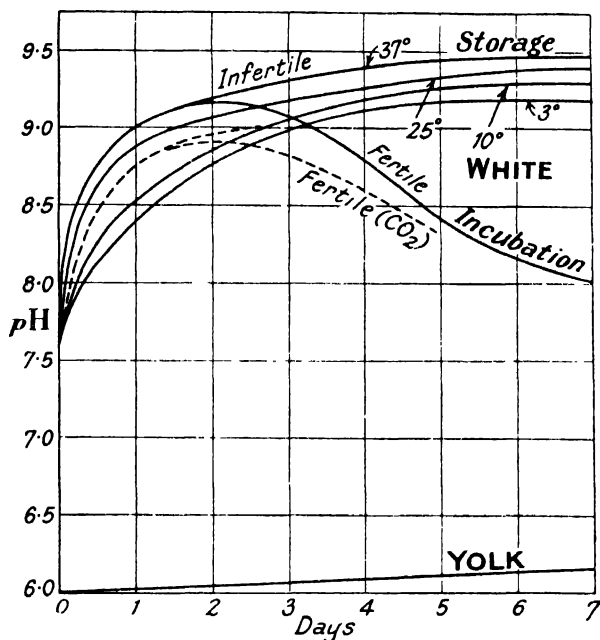
FIG. 178.—Ageing of Hens' Eggs.

at the temperatures, 3°, 10°, 25° and 37° C. respectively, in desic-
cators whose relative humidity was controlled at a little below
80 per cent. and which contained dishes containing a few pieces
of soda lime in order to maintain a low level of carbon dioxide.
It will be seen that the increase in *p*H became greater at the
higher temperatures, whilst storage for periods up to 100 days
at temperatures below 37°, caused the *p*H to rise steadily to a
value of about *p*H 9·7 ; it was repeatedly observed that after
about ten days at 37°, the *p*H values tended to decrease. Tice
(*N.J. State Board of Health*, 1911, Report 35, 275) also found

that the alkalinity as determined by titration underwent decreases after long storage. The curve corresponding to storage at 37° also gives the course taken by the pH of the egg-white of infertile eggs during the first stage of incubation. If fertile, the pH of the egg-white follows the downward trend shown. The broken line corresponds to incubation in air containing a few per cent. of carbon dioxide. Its effect is to lessen the discharge of carbon dioxide and so to prevent the pH reaching the higher maximum. The bottom line represents the change followed by the yolk.

The changes that occur with rising pH take place mainly in the mucin present both in the white and in the yolk. The mucin gel loses its strength and ultimately passes into the sol form. It is thus denatured in much the same way as myosin becomes denatured in meat.

These observations seem to indicate that eggs should be kept at as low a temperature as possible in order to avoid loss of carbon dioxide, the retention of carbon dioxide tending to preserve the eggs. This may be demonstrated by the following points. Storing at 37° C. will cause the pH of the egg-white to rise to 9·25 in two days ; at 16° C. in five days ; and at 2° C. in ten days. Preserving processes such as " oil-dipping " should be carried out very soon after laying. If the oil dipping is done immediately after laying the maximum amount of carbon dioxide will be retained with the consequent maximum preserving effect on the yolk. The application of preserving processes to eggs, after they have lost much carbon dioxide and the pII of the egg-white has been correspondingly raised, results in very little, if any, preservation. Sharp and Powell, however, state that if a little carbon dioxide is allowed to escape before oil dipping, a better condition of the white is obtained in that it does not become so turbid and it will be slightly greater in amount (see also Gueylord and Portier, *Compt. rend.*, 1925, **153**, 1962 ; Schweizer, *Mitt. Lebensmit. Hyg.*, 1929, **20**, 203, 312 ; Romanoff and Romanoff, *Biol. Bull.*, *Marine Biol. Lab.*, 1929, **57**, 300 ; Wladimirov, *Biochem. Zeitsch.*, 1926, **177**, 280 ; Sharp, *Science*, 1929, **69**, 278).

To maintain the pH of the white of eggs as near to its original value as possible, the eggs should be stored in an atmosphere rich in carbon dioxide, 3 per cent. at 0° and 10 per cent. at 20°–25° C. (Moran and Hale, *J. Exp. Biol.*, 1936, **13**, 35, 41 ; Smith, *Food Invest. Bd. Rept.*, 1935, 35).

The stability of foams of egg-white is dependent on pH. Bailey (*Ind. Eng. Chem.*, 1935, **27**, 973) finds that foams produced

by whipping mixtures at pH 6–7 are more stable than those obtained with untreated egg-white, whereas adjustment to pH 5 gives a more voluminous foam from which there is a smaller tendency for the thin white to leak.

CHAPTER XLII

THE IMPORTANCE OF HYDROGEN-ION CONCENTRATION IN BAKING

THE successful production of bread is apt to be regarded as an industry which is dependent chiefly upon the skill of the baker, and to a lesser extent upon the flour available. It might therefore be argued that the baking industry is one of the few which lies outside the possibilities of scientific control, and that the quality of the bread manufactured must necessarily be the result of trial and error. This attitude of mind has undoubtedly been aggravated by the inability of the chemist to delve into the complex nature of the proteins present in flour, and of the enzymic reactions which occur during the preparation of the dough, and later on in the first stages of baking. Though, perhaps, the recent advances made in this special branch of chemistry may not be considered as epoch-making, one thing is certain, that the correlation of the changes in hydrogen-ion concentration during the combination of the proteins with acids and bases, together with the variations in their physical properties, provide in hydrogen-ion concentration measurements a useful aid in the control of baking processes. It is, moreover, a fact that some efforts are now being made to control baking processes on the industrial scale in such a way. Such control applies particularly to the times required for efficient fermentation of the dough before moulding and placing in the oven. It is, of course, futile to prophesy that bakers will adopt these methods in their daily routine, but it is evident that millers are endeavouring to provide, and bakers to use, flours which have been improved as far as their baking properties are concerned by the inclusion of some harmless ingredient, whose initial effect is generally found to raise the hydrogen-ion concentration of the aqueous extract of the flour. Additional improving treatment is very often accorded by the bakers themselves. Such an " improver " is acid calcium phosphate, a variable mixture of mono- and dicalcium phosphate. Formerly, alum was employed for this purpose, and as was pointed out by Jessen-Hansen, its efficacy was undoubtedly due to the appreciable amount of acid set free by hydrolysis, thereby enabling a better loaf to be produced.

In order to make clear that which follows relating to the rôle

played by hydrogen ions in different concentrations some attention will now be directed to flour. Wheat flour comprises colloidal bodies, chiefly starch and proteins, water, and a very small amount of crystalloidal bodies, namely, sugars and mineral matter. According to Kent-Jones (*Modern Cereal Chemistry*, Liverpool, 1927), the different flours and wheats show relatively little variation in their analyses, as shown in Table 216.

TABLE 216

COMPOSITION OF WHEAT AND FLOUR

	Wheat.	Flour.
	Per Cent.	Per Cent.
Starch	63 –71	65–70
Proteins	10 –15	9–14
Water	8 –17	13–15
Cellulose	2 – 3	} 1
Fat	1½– 2	
Sugars	2¼– 3½	2¼
Mineral Matter (ash)	1½– 2	½

The mineral matter, as ash, constitutes from 0·3 to 0·7 per cent. of the flour, and, as the following typical analytical figures show, is made up of phosphoric acid partially neutralised by potash, magnesia, and lime : K_2O 37·04 per cent., MgO 6·12 per cent., CaO 5·53 per cent., Fe_2O_3 and Al_2O_3 0·36 per cent., P_2O_5 49·11 per cent., SO_3 0·40 per cent. (Kent-Jones). Despite the fact that analyses of flours show only slight variations, flours differ widely in their baking properties, which have been traced mainly to the colloidal properties of the proteins, and also to the changes in these properties which occur by varying the hydrogen-ion concentration. Flours have come to be known as either " strong " or " weak " according as they bake well or badly. Thus Humphries and Biffen (*J. Agric. Sci.*, 1907, **1**, 1) defined a " strong wheat " as being one " which yields flour capable of making large, well-piled loaves." Such a definition is vague, and should include the condition of giving a satisfactory texture. Moreover, the formation of well-piled loaves may be due merely to an inadequacy of diastatic action to produce the necessary sugars for the maintenance of the activity of the yeast, in which case the texture would be inferior. Sharp and Gortner (*J. Physical Chem.*, 1922, **26**, 101) suggest that there are " at least three classes of weak flour," having, either

(1) Weakness due to the inferior quality of the gluten, though present in an adequate quantity,

(2) Weakness due to an inadequate quantity of good gluten ; or

(3) Weakness due to factors influencing yeast activity.

Much of the starch present in flour appears to resist decomposition during dough making on account of the difficulty in rupturing the coverings of the starch granules. The ease with which the starch contents of the various flours may thereby become available to diastatic decomposition provides, in the opinion of Collatz (*Amer. Inst. Baking*, 1922, *Bull.* No. 9), an important point of difference between strong and weak flours, for the greater amount of sugars formed in strong flours permits of a plentiful supply of carbon dioxide being developed during fermentation, which is necessary to raise the dough.

On storage the pH of dry flour tends to fall to 5·7 but, according to Lausten (*Milling*, 1952, **119**, 40), it may occasionally fall to as low as pH 3·8, owing to the formation of lactic acid, apparently not through bacterial action. Because the reaction may be inhibited, but not stopped, by the inclusion of either calcium carbonate or sodium bicarbonate in the flour, it is thought that the improvement which occurs in the baking qualities of flour on storage might be attributed to lactic acid, which is itself employed to improve certain types of flour.

The production of well-piled loaves necessitates the formation of dough of such a fine texture as not to be readily pervious to gas ; in other words, to have a good gas-retaining property, and moreover, to be able to retain it during the early stages of baking in the oven. This property is intimately connected with the proteins of the flour. The chief proteins are *gliadin* and *glutenin*, the latter imparting solidity, whereas the former adheres to the glutenin to form a coherent mass. On adding water to flour, hydration ensues with the formation of a colloidal complex, *gluten*, from these proteins. There is very little difference in the percentage compositions of gliadin and glutenin, but differences occur in their physical properties. Gliadin can be extracted by means of 70 per cent. alcohol. The gas retention of doughs then depends upon the dispersion, coherence, elasticity and the imbibition water content of the gluten, and these factors have been found to be influenced by acids and salts in various concentrations. In order that gliadin, which according to Lüers (*Kolloid Z.*, 1919, **25**, 177, 230) is the more important protein, may yield the best baking results, a certain degree of swelling must be attained, and this can be produced if due regard be paid to such factors as hydrogen-ion concentration, electrolytes, temperature and time. Bungerberg de Jong (*Trans. Faraday Soc.*, 1932, **28**, 798) found, by

means of turbidity experiments, that the isoelectric point of gliadin is at *p*H 6·3–6·6 and that of glutenin is at *p*H 5·3–5·4. Maximum turbidities were observed at these *p*H values.

Two objects have to be kept in mind in the milling of flour, namely (*a*) to obtain the maximum yield of flour from the wheat— about 10 per cent. is generally lost—and (*b*) to produce a flour having the most satisfactory baking properties. Various treatments may be resorted to in the conditioning of the wheat, such as drying in the case of damp wheats, adding water, subjection to a suitable temperature for a certain length of time, and finally grinding. Conditioning, though originally introduced in order to toughen the bran to prevent it being pulverised during grinding, so as to effect a better separation from the endosperm, may have an important effect upon the colloidal properties of the flour proteins and thereby influence the baking strength of the flour. Tague (*J. Agric. Res.*, 1920, **20**, 271) has investigated the changes involved during the tempering of wheat by measuring the *p*H, titratable acidity, titratable nitrogen by the Sørensen Formol method, and the amount of water-soluble phosphorus. He concluded that the changes undergone in producing wheat of good milling quality were physical in character and occurred after maintaining the wheat at 20° to 25° C. for 48 hours so that it had a moisture-content of 15½ per cent. Increase in temperature gave increased hydrogen-ion concentration, titratable acidity, titratable nitrogen and a greater quantity of water-soluble phosphorus. A temperature of 5° C. gave a wheat of higher *p*H, but one which was brittle and hard, whereas 40° C. gave a sticky product. Geddes (*Canad. J. Res.*, 1930, **2**, 195) found that the heat-treatment of wheat-germ causes a marked lowering of the *p*H value of the aqueous extract and also a decrease in the Wijs Iodine Value of the residue after extracting with ether. Hence though such treatment is harmful to the gluten, it has a marked influence in reducing the deleterious effects of the germ constituents. Low-grade flours may therefore undergo considerable improvement in their baking qualities, despite the possible injury to the gluten on heat-treatment. Kent-Jones (*Modern Cereal Chemistry*, 1927, p. 294) states, however, that "experience has shown that the best course is to differentiate entirely between any strengthening process and any conditioning process," and that the latter operation "should be restricted to getting the wheat into as nice a milling state as possible, and no attempt should be made to perform the heat-treatment in the same operation." As the processes involved in milling bring about a change in the physical state of the flour, it could hardly be expected that *p*H determinations could provide

any means of control—and this is in agreement with the experience of Weaver (*Cereal Chem.*, 1925, **2**, 209).

Bactericidal action in flour is much more effectively counter-acted by previously adjusting the pH of the flour to a value below pH 4·5 before treating either with steam or with chemical preserva-tives (Cruess, *Ind. Eng. Chem.*, 1932, **24**, 648).

pH of Flour Extracts.

The hydrogen-ion concentration of flours is largely determined by the protein substances and phosphates which pass into the aqueous extract. These behave as very efficient buffers and usually maintain a hydrion-concentration of a little above pH 6. The pH's of aqueous extracts of flours were investigated by Bailey and Peterson (*Ind. Eng. Chem.*, 1921, **13**, 916), who found that the time allowed for the extraction and the temperature at which it was carried out had scarcely any effect upon the pH. This will be seen from the results given in Table 217, which are typical data. Their extracts were made by treating 1 part of flour with 5 parts of water.

TABLE 217

EFFECT OF TEMPERATURE ON THE pH OF FLOUR EXTRACTS

Temperature.	Flour.	pH of Extract	Flour.	pH of Extract.
0° C.	Patent	6·10–6·09	Clear	6·29–6·27
25° C.	,,	6·05–6·05	,,	6·30–6·31
40° C.	,,	6·00–5·99	,,	6·29–6·30
60° C.	,,	6·04–6·04	,,	6·25–6·25

The ranges of pH correspond to extracts prepared by allowing 1, 2, 4, and 6 hours. Furthermore, Kent-Jones (*loc. cit.*) has shown that it is immaterial what proportion of flour is used in preparing the extract, and also whether the pH determination is made on the filtered extract or on the flour suspension itself. These hydrogen-ion concentrations should provide some valuable indication of the baking strengths of the flours, for they represent equilibrium conditions of the reactions which are set up between the flours and the aqueous extracts. These equilibria can only be established at the flour-water interface, and they in turn determine the degree of dispersion and viscosity of the sus-pensions—both factors being of importance in the production of a satisfactory dough. It is in facilitating the rapid attainment of equilibrium between flour particles and water that (*a*) the problem

of efficient grinding to give them a large surface, and (b) the moisture contents become of great importance. It is not surprising therefore that the better quality flours, i.e., better as regards baking strength, impart to the aqueous extracts greater hydrogen-ion concentrations than do the poorer quality flours. Thus Bailey and Peterson's data (loc. cit.) given in Table 218 show that the better grades of flour give the lower pH. They possess incidentally, as shown, the lower ash contents, and as the inorganic constituents of flour comprise soluble phosphates, it is reasonable to imagine that the smaller the ash-content the smaller will be the buffer

TABLE 218

pH AND QUALITY OF FLOUR

Grade of Flour.	pH.	Per Cent. Ash	Grade of Flour.	pH	Per Cent. Ash.
Patent	6·02	0·40	3rd Break . .	6·22	0·67
1st Middlings . .	6·07	0·44	1st Clear . . .	6·40	0·83
2nd Middlings .	6·10	0·45	4th Middlings .	6·42	1·17
3rd Middlings	6·22	0·55	1st Break . . .	6·24	1·34
2nd Break . . .	6·25	0·58	2nd Break . .	6·44	2·38
5th Middlings. .	6·31	0·61			

action on the hydrogen-ion concentration of the flour extract. This may explain the lower pH of the better grades of flour as shown in the above table. Similar data were obtained by Kent-Jones (loc. cit.) for flours produced in England which are as follow : Commercial Patent, pH 5·90 ; English (straight run), pH 6·28 ; Commercial Bakers' (straight run), pH 6·20 ; and Low Grade Commercial, pH 6·50.

Buffer Action of Flours.

The ease with which the pH of a flour can be lowered by the acid developed during the fermentation process is one factor on which the efficiency of that process depends. This is the same as saying that the proportion of buffers present in a flour should be small. Fig. 179 gives typical electrometric titration curves, using the hydrogen electrode, of 100 c.c. of aqueous extracts of different grades of flours with 0·02 N-HCl and 0·02 N-NaOH. They are taken from Bailey and Peterson's paper, and refer to the flours given in Table 217. The numbers enclosed in brackets are the percentage ash-contents. It will be observed that the best grade—Patent—having the lowest ash, 0·40 per cent., gave rise to the greatest change in pH when either hydrochloric acid or sodium hydroxide was added, and that these effects became

less with the increasing content of mineral matter. As mentioned previously much of the mineral matter comprises acid phosphates. The second dissociation constant of phosphoric acid is $1\cdot4 \times 10^{-7}$, and therefore the pH corresponding to half-neutralisation of the second stage will be equal to pK$_2$, *i.e.*, $6\cdot85$. This will be the pH at which the maximum buffer action will be exerted, so that
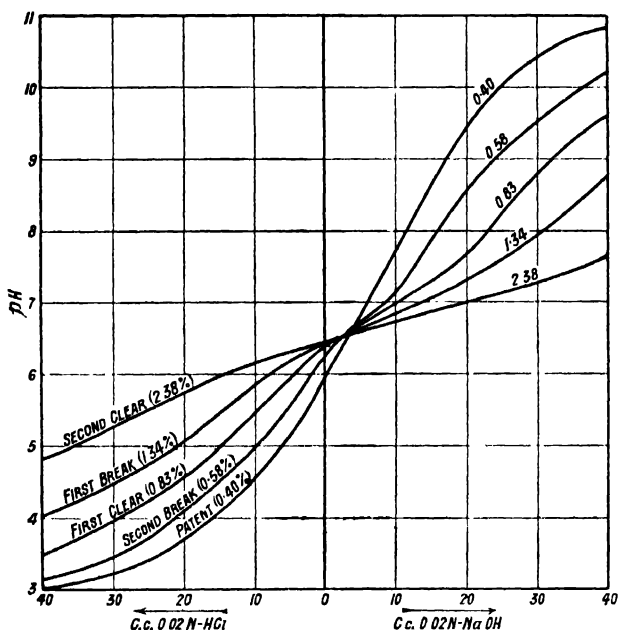
Fig. 179.—Hydrogen Electrode Titration Curves of Flour Extracts.

if much phosphoric acid be present additions of either acid or alkali will cause comparatively small pH changes (compare phosphoric acid curve on p. 294). These remarks explain both the positions and the shapes of Bailey and Peterson's curves. Kent-Jones records the buffer action of flours by taking the pH of a water extract, then again after 10 c.c. 0·01 N-lactic acid has been added to 100 c.c. of extract, and multiplying the diminution in pH by 10 (*cf.* Holm and Crewe, *Cereal Chem.*, 1930, **7**, 49). Fisher and Halton (*Cereal Chem.*, 1928, **5**, 445 ; 1929, **6**, 18, 97) claim that the pH value of flours is not a factor of great importance in determining dough or loaf quality, though they state that increased hydrogen-ion concentration may produce increased dough toughness, more pronounced flavour, and improved quality of crumb.

*p*H and Fermentation.•

Flour contains a certain amount of diastase, produced by slight germination of the wheat, which during the dough preparation brings about the conversion of the available starch into maltose, and this, in turn, through the enzyme maltase, passes into dextrose.
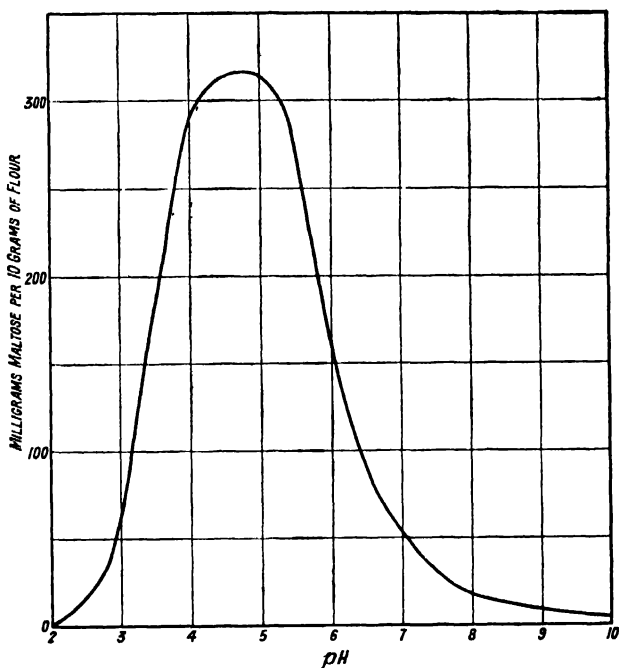
FIG. 180.—*p*H and Activity of Wheat Flour Diastase.

This is particularly the case when either malt-extract or malt-flour is added in order to supplement, when necessary, the diastatic activity. An adequate supply of these sugars, dextrose and maltose, in the dough is required to support the activity of the zymase in the added yeast. Zymase breaks down the sugar to form carbon dioxide and ethyl alcohol, so that the dough becomes aerated and raised by the gas and alcohol vapour. Rumsey (*Amer. Inst. Baking*, 1922, *Bull.* No. 8) has investigated the influence of hydrogen-ion concentration on the activity of wheat flour diastase. His data, plotted in Fig. 180, show the relationship between the *p*H and the amounts of maltose formed when 10 grams of a flour, after having been brought to the desired

pH by the addition of acid or alkali, were digested at 27° C. for
one hour. The maximum activity occurred at a pH between 4·7
and 4·8, with a broader range between pH 4·0 and 5·3. This
optimum pH, 4·7 to 5·0, is also that found by Sherman, Thomas,
and Baldwin (*J. Amer. Chem. Soc.*, 1919, **41**, 231) for the activity
of the diastase of malted barley. It should be stated that the
temperature 27° C. was chosen because it is that at which fer-
mentation is effected. Increased activity occurs with longer
time, but at this temperature the increase after 60 minutes'
digestion is uniform and gradual. With higher temperatures
the increase in maltose formation becomes much more rapid.
Working with one-hour digestions at different temperatures
it was found that the greatest activity occurred at 63·5° C.
Collatz (*Amer. Inst. Baking*, 1922, *Bull.* No. 9) made similar
observations with malt flour and found that the optimum pH
for the amylase contained therein was pH 4·26, though the
activity was still considerable between pH 3·5 and 5·5. Care
must be exercised in the use of malt extract to employ just that
quantity which will give the requisite amount of diastatic activity.
Should it be excessive the dough becomes sticky and runs, and
on baking may yield a loaf sticky in the centre, or the dough may
even fail to bake.

Hydrion concentrations play an important part in the ferment-
ing stage. Thus the maximum rate of fermentation is reached
at pH 5·0, and also the proteolytic enzymes in the yeast act
best in the neighbourhood of pH 5·0. Though much of the gas-
retaining power of the dough is inherent in the quality of the
gluten, which is influenced by both the quality and quantity of its
glutenin, much will depend upon any further change in the dough
brought about through the action of protease ; if this has not
been too great it may have a beneficial effect in softening the dough.
Another reason why doughing should be carried out at a pH near
to 5 is that the isoelectric point of flour-proteins is situated in its
vicinity, and this accounts for the fact that it is here that the dough
is generally most coherent and elastic.

The variations in hydrogen-ion concentration during the fer-
mentation of doughs have been studied by Bailey and Sherwood
(*Ind. Eng. Chem.*, 1923, **15**, 624) with very interesting results.
They found that the hydrion concentration increases at a fairly
uniform rate in bread doughs fermented under fixed conditions,
and increasing the temperature, as in " proving," when the dough
is finally moulded and placed in the oven, accelerates the rate of
increase. This increase in true acidity is due to the production of
organic acids by the various yeast enzymes. " Sponge doughs,"

in contrast with the ordinary " straight doughs," are made with
a greater proportion of water by mixing with it at first a portion
only of the flour, and then incorporating the remaining quantity
of flour after fermentation has proceeded for a fairly long period.
These doughs undergo a more rapid increase in the concentration
of hydrogen ions.   The rate of increase in hydrion concentration
appears to depend upon (a) the grade of flour, the doughs formed
from high-grade or patent doughs changing more rapidly in pH
than do those prepared from low-grade or clear flours, and (b) the
consistency of the dough.   Table 219 gives the change in pH
found by Bailey and Sherwood.

TABLE 219

pH OF FERMENTING DOUGHS

Time of Fermentation (Minutes).	Patent. pH.	Clear. pH.	I pH.	II pH.	With Acid Phosphates and Malt Extract.	
					I pH.	II pH.
0	5·59	5·85	5·43	5·64	5·36	5·54
120	5·44	5·65	5·22	5·38	4·99	5·28
240	5·20	5·48	5·01	5·20	4·73	5·01
360	4·83	5·27	4·89	5·04	4·70	4·85

It will be observed that the dough made from clear, low-grade
flour, owing to its great buffer content, did not undergo change
in pH as quickly as did the patent flour dough.   Yet it is found
by practical experience that low grades cannot be subjected to
fermentation for as long as the better grades, and therefore they
cannot acquire that pH which permits of maximum yeast activity.
Thus, in the case of the patent and clear doughs Bailey and Sher-
wood state that patent doughs are ready for moulding in about
270 minutes, whereas the time for clear doughs is 225 minutes.
Hence, to see if doughs could be made to acquire a higher concen-
tration of hydrogen ions, they added to doughs I and II a mixture
of acid phosphates, phosphoric acid and malt extract, and obtained
more acid doughs (see Table 219) which were ready for moulding
in 300 minutes and which led also to an improvement in colour,
grain and texture of the resulting loaves.   Moreover, with such
a pH the yeast activity was so enhanced that the volume of yeast
used could be reduced without impairing the bread.   Their data
corresponding to the changes in pH in a typical commercial sponge
dough show that the sponge, which was fermented, started with a
pH $= 5·71$ and fell to pH 4·94 after 340 minutes, when it was

ready to be returned to the mixer. "Owing to the addition of more flour the finished dough became pH 5·53 and the bread pH 5·42. In a straight dough the pH varied continuously from 6·16 down to 5·66 in the baked loaf. Rumsey (*Amer. Inst. Baking*, 1922, *Bull.* No. 8) points out that the optimum hydrogen-ion concentration for flour diastase, pH 4·7, is seldom reached during the fermentation of a normal dough, though the increase in acidity during fermentation in the range of pH 6 to 5 has the effect of considerably increasing the production of maltose toward the latter part of the fermentation process. As temperature has a considerable effect in the control of diastatic action in dough, the higher the temperature of " proving," coupled with the lower pH, make the effect of diastase more pronounced during the later stages of fermentation. This enables the diastase to convert starch into sufficient reducing sugars for the yeast to complete the aeration of the loaves. It is also largely upon this stage that the kind of " oven-spring " obtained depends, for if the gas production in the dough just before placing in the oven is poor there will result small, solid, unsatisfactory loaves.

There is another advantage to be obtained by bringing the dough as near as possible to pH 5 in the fermentation process. It happens that the activity of rope-producing organisms, *e.g.*, *B. mesentericus*, becomes almost completely prevented. Stuchlik (*Chem. Obzor.*, 1935, **10**, 4) found that rope bacilli will not grow in media below pH 4·6. These bacteria flourish in doughs of higher pH and have been found to produce ropy doughs between pH 5·5 to 6·0. The advisability of aiming at pH 5 in dough making was first advocated by Jessen-Hansen (*Compt. rend. Lab. Carlsberg*, 1911, **10**, 170) as far back as 1911, and it has since been confirmed by Cohn and Henderson (*Science*, 1918, **48**, 501) ; Dearsley (*N.Z. J. Sci. Tech.*, 1925, **8**, 34) ; and Dunlap (*J. Amer. Assoc. Cereal Chemist*, 1922, **7**, 2 ; *Cereal Chem.*, 1926, **3**, 201).

The use of skim milk in baking appears to be related to the increased buffer action thereby introduced (Bailey and St. John, *Cereal Chem.*, 1929, **51**, 140). The present tendency of bakers to use larger quantities of milk solids favours the growth of rope organisms, for, as Hoffman, Schweitzer and Dalby (*Ind. Eng. Chem.*, 1937, **29**, 464) state, the introduction of these milk solids raises the pH to 5·37-5·70.

Reference will now be made to the classical experiments of Jessen-Hansen concerning the relationship which exists between the pH of flours, adjusted by the addition of different acids, and the sizes of the loaves which they produce when prepared by an experienced baker. Typical curves, constructed from some of

his many data for different•acids, are given in Fig. 181 expressing
the variation in " specific volume " with *p*H.   The term " specific
volume " refers to the volume in cubic centimetres of 1 gram
of bread.   It will be observed that the maximum size of loaf was
obtained with flours adjusted to *p*H 4·6 to 5·0.   The differences
in the actual maximum specific volumes given by the different
acids, lactic, acetic, hydrochloric, and phosphoric, must be
regarded as due to other factors, though the variation in loaf size
is evidently the result of the *p*H's of the flours.   He also traced
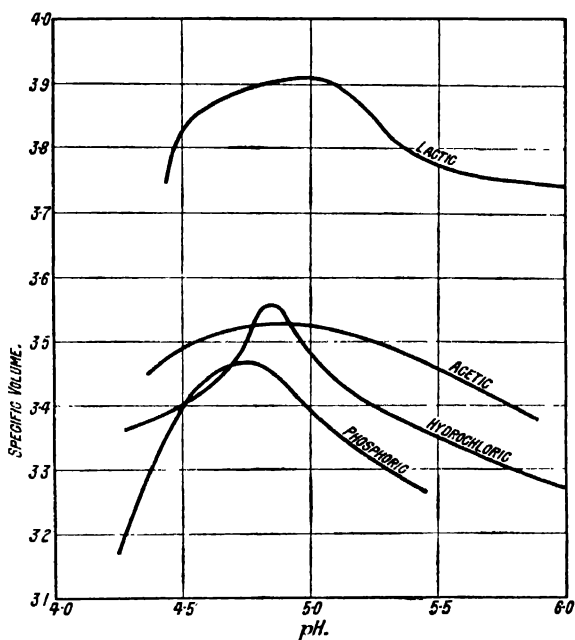
FIG. 181.—Size of Loaf and *p*H.

the efficacy of alum as an improver to the decrease in *p*H set up
in the flour.
    The agents sometimes used for bleaching flour may cause
increased acidity.   This applies to such substances as chlorine,
nitrogen tetroxide, nitrogen trichloride, and nitrosyl chloride.
Bruère (*Ann. Fal.*, 1925, **18**, 161) suggests that *p*H measurement
may serve as a means of detecting chlorine in flours.   ,
    The increase in the size of a moulded loaf after placing in the
oven is due to the low *p*H attained in the dough and to the en-
hanced enzymic activity which occurs with increased temperature.

The greater volume of carbon dioxide resulting therefrom inflates the dough, which, provided the gluten is of satisfactory quality, will enable the dough to retain the gas until the baking process is nearing completion. Though the " oven-spring " actually produced depends upon such factors as the quality of gluten, the activity of the various enzymes, amylolytic and proteolytic, the kneading and moulding, there is no doubt that many of these factors are themselves dependent upon the original pH of the flour and its buffer action, *i.e.*, the resistance which it offers to changes in hydrogen concentration. Dunlap (*loc. cit.*) states that a flour having a pH of 5·7 to 5·9 will give a splendid " oven-spring." Improvers, such as acid calcium phosphate and ammonium sulphate, tend to diminish the pH of flour. The physico-chemical processes involved in baking include the denaturation of the protein, a process which, as shown by the work of Sørensen, is favoured by a high concentration of hydrogen ions, and the subsequent flocculation and precipitation of the denatured protein. This, according to Sørensen (*Ann. Brass. et Dist.*, 1926, **25,** 65) takes place more rapidly at an optimum pH of 4·8.

Harrell (*Cereal Chem.*, 1927, **4,** 423) has called attention to the fact that as a rule the lowering of pH gives a much whiter bread, and for that reason sponge dough loaves are whiter than straight dough loaves. Then again, both flavour and taste of bread have some connexion with the values of the flour and dough pH.

In view of the many points which may influence the efficiency of baking, it appears probable that, though pH does provide a valuable asset for control, the precise pH's to be attained in doughing must be fixed for each class of flour after it has been examined for such qualities as buffer content, diastatic power, gluten quality, etc.

One of the major problems in cake making is the " curdling " or breaking down of the cake batter. This is caused by the pH of the medium approaching the isoelectric point of egg-white, pH 4·8, at which egg-albumin tends to precipitate. Grewe (*Ind. Eng. Chem.*, 1938, **30,** 719), using a buffer-system consisting of sodium bicarbonate and potassium hydrogen tartrate, found that when either butter or butter-oil was used the stability of the batter increased to a maximum at pH 6·0–6·5, but that with hydrogenated fat the stability greatly increased with increasing pH.

Regarding the flavourings used in biscuit manufacture, Gilmer, Kinder and Bohn (*Cereal Chem.*, 1936, **13,** 421) found that most

flavours, except coumarin are destroyed above pH 7, but that they are substantially retained below pH 6·5.

Some attention has been directed to the effect of pH in the manufacture of baker's yeast. In view of the greater pH control afforded during the decomposition of urea when used as a nutrient, Frey, Schultz and Harrison (U.S.P. 1,814,210) and Epstein (U.S.P. 1,858,488) advocate its inclusion in the fermenting molasses solution. The initial pH suggested by Epstein is pH 6–7, whereas that by Frey *et al.* is pH 4·2–4·5. The International Yeast Co. and Frey (B.P. 390,114) use $NH_4H_2PO_4$ and control the pH at 4·5–5·0 by the occasional addition of ammonia.

CHAPTER XLIII

WATER PURIFICATION, CORROSION, AND SEWAGE DISPOSAL

THE introduction of the control of hydrogen-ion concentration of water during purification dates from 1921, when Wolman and Hannan (*Chem. and Met. Eng.*, 1921, **24**, April) directed attention to its importance. The chief use lies in the control of clarification processes, involving the addition of either alum or iron salts or both, to turbid and coloured waters, and in the case of boiler-feed water to establishing a pH value which will diminish its corrosive action. Another point of importance in regard to public water supply is the fact that water of low pH is apt to assist the growth of iron-bacteria, which cause incrustation of the pipes and may especially attack cast iron, thereby inducing a " spongy disease " (*cf.* Ellis, *Engineering*, 1921, **112**, 457).

The pH values of typical natural waters are recorded in Table 220, which is taken from a paper by Atkins (*Sci. Proc. Roy. Dublin Soc.*, 1930, **19**, 455). The reaction of water is largely due to equilibria between free carbon dioxide and bicarbonate ions, kept in solution in conjunction with calcium and magnesium ions, so much so that Greenfield and Baker (*Ind. Eng. Chem.*, 1920, **12**, 989) have evolved a method by which the pH of natural waters up to pH 8 may be calculated with considerable accuracy from titrations of the free carbonic acid using phenolphthalein, and of the bicarbonate with hydrochloric acid to methyl orange. According to Kolthoff (*Z. Untersuch. Nahr-Genuss.*, 1922, **43**, 184) the pH of a saturated solution of calcium carbonate is 10·2, and the author has found that 0·001 M.-$CaSO_4$ solution does not yield a precipitate with 0·01 N-Na_2CO_3 even though a pH of 10·3 is attained. Using 0·01 M.-$CaSO_4$ and 0·1 N-Na_2CO_3, however, precipitation began at this stage.

Sea-water generally has a higher pH value. Thus, the water near the British Isles is about pH 8·2, though it undergoes seasonal variations due to the photosynthetic action of plankton. It has been shown that the greater part of the alkalinity of sea-water is produced by the more soluble carbonate, that of magnesium, but W. R. G. Atkins (*Sci. Proc. Roy. Dublin Soc.*, 1922, **16**,

TABLE 220

pH OF NATURAL WATERS

Source.	pH.	Notes.
Lake Kawah Idyen, Java, a crater lake in Het Idyen Plateau.	1·5	Acidity due to sulphur acids.
Water in black peat . . .	4	A little non-volatile acid.
Water in brown moorland peat	4·5	Acid largely CO_2
Rain in open country . . .	5·9	——
Moorland stream (Dartmoor)	6·4	Value increases after each waterfall, as CO_2 is lost to air.
Springs in calcareous regions	6·0–6·6	Varying with relative proportions of calcium bicarbonate and free CO_2.
River water, non-calcareous .	6·5–7·0	Also similar lakes.
River water, calcareous . .	8·0–8·4	Also similar lakes.
Small ponds, among weeds .	9·6	During active photosynthesis.
Sea-water, surface	8·1–8·4	High values in the tropics.
Sea-water, in pools . . .	8·6	During active photosynthesis.
Sea-water, 2000 m., Atlantic Ocean	7·95	——
Sea-water, 1000 m., Black Sea	7·26	H_2S below 180 m.
Water in alkali soil, Sudan .	10·0	Sodium carbonate present.

380) has found as high a value as pH 9·7, probably due to the removal of carbon dioxide by algæ This considerable buffer action, caused by $HCO_3' \rightleftharpoons H^· + CO_3''$, is so great in natural waters and soil extracts that it prevents the attainment of a pH value of 10·4, required for the precipitation of the magnesium hydroxide which they contain. The expulsion of carbon dioxide from tap-water by boiling leads to a higher pH value. Thus Atkins (*Nature*, 1921, **108**, 339) obtained an increase from pH 6·8 to pH 8·5.

It is difficult to obtain as high a pH as 10, though when water has been so adjusted the small sodium hydroxide content has a deleterious effect when used for steam raising in rendering the metal of the boiler brittle. According to Parr and Straub (*Ind. Eng. Chem.*, 1927, **19**, 620) caustic embrittlement of boilers, resulting in cracks and crevices, occurs with those waters which contained high proportions of the carbonates of sodium, magnesium, and calcium. Such water, though containing too little free alkali to cause direct embrittlement, has been found to lead to the production of solid caustic soda in the cracks and crevices. It is probable that water which has been softened either by sodium carbonate or by the action of permutite will contain sodium salts in fairly high concentrations.

In the estimation of carbonates in water with hydrochloric acid to the first tinge of orange of methyl orange, *i.e.*, at pH 4·6, high results will be obtained if the concentration of the liberated carbonic acid exceeds 0·0012 M., or 73 p.p.m. of CO_2. Whilst the pH corresponding to the first or bicarbonate end-point when a carbonate is titrated with 0·02 N.HCl remains at 8·35 irrespective of the concentration of the soluble carbonate, the pH of the second end-point varies from 4·63 to 4·98 depending on the concentration, c, of the carbon dioxide then present in the water.

Thus as
$$H_2CO_3 \rightleftharpoons H^{\cdot} + HCO_3',$$
$$Ka_1 = \frac{[H^{\cdot}][HCO_3']}{[H_2CO_3]} = \frac{[H^{\cdot}]^2}{c}$$
whence
$$pH = \tfrac{1}{2}pKa_1 - \tfrac{1}{2}\log_{10} c$$

If the normality of the hydrochloric acid used is N, and x c.c. of the acid are required to bring the solution to the first end-point, *i.e.* to phenolphthalein, and a further y c.c. to titrate the solution from the first to the second end-point, and the volume of the water taken is v c.c, then
$$c = \frac{y.N}{v + x + y}$$
whence
$$pH = \tfrac{1}{2}pKa_2 - \tfrac{1}{2}\log N + \tfrac{1}{2}\log\left(\frac{v + x + y}{y}\right),$$
thus enabling the precise end-point pH to be calculated. Cooper (*Ind. Eng. Chem., Anal. Edn.*, 1941, **13**, 466) proved the accuracy of this expression by titrating solutions of mixtures of Na_2CO_3 and $NaHCO_3$ ranging from 0·151 to 1·567 millimols per litre of the former and from 0·049 to 0·286 of the latter. For these solutions the end-point varied from pH 4·58 to pH 4·93.

To locate the end-points more accurately he modified the usual screened indicator (Vol. I, p. 440) of Methyl Red and Bromocresol Green. In 100 c.c. of 95 per cent. alcohol, 0·02 gram of Methyl Red and 0·10 gram of Bromocresol Green are dissolved. Of this solution 3 drops are added to 100–250 c.c. of water. The sequence of colours are :

pH 5·2 and above   Blue with a trace of Green
pH 5·0   Light Blue with Lavender Grey
pH 4·8   Light Pink Grey with a tinge of Blue
pH 4·6   Light Pink
Below pH 4·6   Pink or Rose.

The figures in Table 221 show the extent of the error introduced by Methyl Orange alone, the screened indicator as modified as used by Cooper, the Methyl Orange—xylene cyanole indicator of Hickman and Linstead (Vol. I, p. 441).

•TABLE 221

PERCENTAGE ERRORS

CO_2 : p.p.m.	30	50	70	100	150	250
Methyl Orange	4·5	1·8	0·5	0·4	0·1	0·1
Methyl Orange—Xylene Cyanole	5·3	3·2	2·1	1·5	1·4	0·6
Methyl Red—Bromocresol Green	0·4	0	0	0·2	0·2	0·2

In the previous paragraphs it was tacitly assumed that the water contained no other substance that would react with acid or alkali within the pH range 8·3–5, but this is not always the case especially with moorland water which often contains organic matter. · To allow for such substances, McKinney (*Ind. Eng. Chem., Anal. Edn.*, 1944, **16**, 315) titrates 100 c.c. of water, to which 0·4 c.c. of a mixed indicator consisting of Methyl Red and *O*-cresolphthalein had been added, with either 0·02 N.HCl or 0·02 N.NaOH to pH 8·5, and thence to pH ·5 with 0·02 N.HCl after which a 20 per cent. excess of acid is added. After vigorously boiling for 2 minutes, to drive off the carbon dioxide, the solution is cooled to room temperature and titrated with 0·02 N.NaOH to pH 8·5 and then back-titrated to pH 5 with 0·02 N.HCl. From the two sets of titres the carbon dioxide content can be calculated.

In the permutite method of water-softening an exchange takes place between the sodium in permutite (sodium alumino-silicate) and the calcium and magnesium in the salts present in water. The revival of the calcium and magnesium permutite ultimately formed is effected by treatment with a saturated solution of common salt. In this method of softening, the softened water instead of having its bicarbonate, chloride and sulphate in combination with calcium and magnesium has them in combination with sodium. The hydrogen-ion concentration of brine used in reviving used permutites is an important factor, so also is the pH of the water undergoing softening. Brine having too high a pH value, above pH 7·8, leads to unsatisfactory results, and too low a pH causes solvent action on the agent (Sweeney and Riley, *Ind. Eng. Chem.*, 1926, **18**, 1214). Water with a pH higher than about 8·3 (*i.e.*, the pH at which phenolphthalein begins to redden) leads to the gradual peptisation of the silica and thus to the eventual disintegration of zeolites, whereas acid waters diminish their base-exchange capacity. According to Behrman and

Gustafson (*ibid.*, 1936, **28**, 1279), there is a fall of about one *p*H unit in the effluent, after passing through the regenerated zeolite. Despite the fact that zeolite action is restricted to a *p*H range from 6 to 8, which is lower than that at which magnesium hydroxide or basic carbonate becomes precipitable, the formation of insoluble calcium and magnesium complexes with the permutite causes the removal of a large proportion of these metals. See also Walker and Collins (*ibid.*, 1929, **21**, 1020).

We shall now consider the advantages which arise from the *p*H control of the alum and the more usual aluminium sulphate treatment of water. The maximum clarification depends upon the nature of the aluminium hydroxide precipitate formed in the water on the subsequent treatment, when necessary, with lime or some other alkali. Another point is that of the economical use of alum. Precipitation is determined largely by the *p*H set up, though as we have seen in Chapter XXIV the actual appearance of the precipitate is dependent upon the nature of the anion in solution. Thus precipitation from an aluminium sulphate solution begins at about *p*H 4·1, whereas from chloride solutions though the *p*H curves are similar, the formation of precipitates is delayed until about *p*H 6. Moreover, organic radicals sometimes prevent the separation of a precipitate completely.

The results of Theriault and Clark (*U.S. Pub. Health Rep.*, 1923, 181) show that as the alum solutions become increasingly dilute, the *p*H range in which rapid flocculation occurs becomes narrower, giving a maximum flocculation at *p*H 5·5. Hatfield (*J. Amer. Water Works Assoc.*, 1924, **11**, 554) found the maximum rate of flocculation with alum in Lake St. Clair water took place at *p*H 6·1 to 6·3, but the filter effluent was found to be free from soluble aluminium salts over a wider range, from *p*H 5·8 to *p*H 7·5. Alum is recommended by Francis (*Surveyor*, 1935, **88**, 33) for the removal of colour from peaty water (Capetown) at *p*H 4·9. Black and Bartow (*Ind. Eng. Chem.*, 1933, **25**, 811) state that the rate of " floc " formation in the presence of sodium sulphate with aluminium sulphate and alkali is rapid between *p*H 5 and 7. Sodium chloride restricts the range of rapid " floc " formation to *p*H 6·5–7·5, so also does the bicarbonate ion, the range then being *p*H 7·0–7·5.

Miller (*U.S. Pub. Health Rep.*, 1925, 351) has carried out some very useful work on the nature of " alum floc," and also on the amounts precipitated at different *p*H values from very dilute solutions containing various anions. His results are summarised in Fig. 182. The continuous curves refer to precipitations from solutions 0·005 Molar with respect to Al. The precipitant was

sodium hydroxide, except •in one instance when potassium car-
bonate was used. The discontinuous curves correspond to pre-
cipitations from 0·0005 M.-Al solutions with sodium hydroxide.
The zone of maximum insolubility •of the aluminium hydroxide
precipitated from a sulphate solution was considerably more
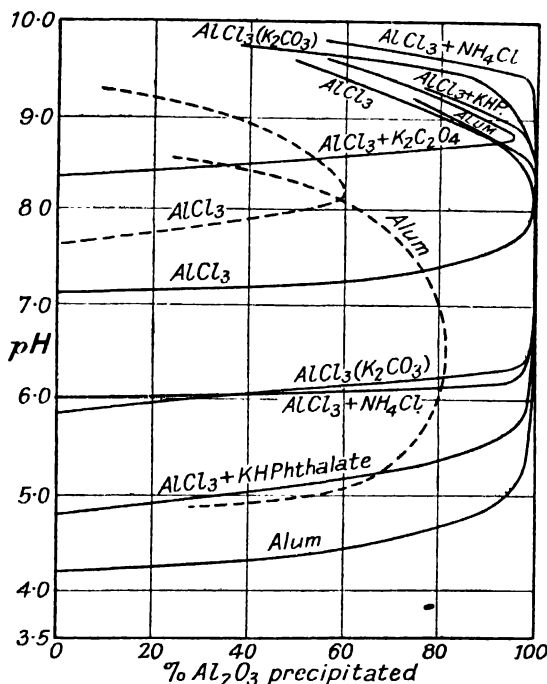
FIG. 182.—Effect of pH and Anions on the Precipitation of " Alum Floc.'

extensive than that obtained from a chloride solution. The
widening of the zone by the inclusion of ammonium chloride
in the solution is noteworthy, and explains the importance of that
salt in flocculating colloidal alumina in analytical procedures.
The effect of dilution is also clearly indicated, not only in reducing
the insolubility zone, but also in permitting a certain amount of
aluminium hydroxide to remain in solution, presumably in
colloidal form. Miller found that the rate of precipitate formation
from a very dilute alum solution attained a maximum value at
about pH 5·5, whereas from a chloride solution this occurred at
pH 8·0. This demonstrates the strong coagulating power of the
sulphate ion.

For the successful clarification of water by alum three factors must be considered : (1) the minimum amount of alum to be added must be known, (2) there must be present an anion which will readily promote coagulation, and (3) the correct pH value for a particular water must be established. As regards the first factor a saving may be effected by merely adding the minimum amounts and adjusting the water to the required pH value by the addition of sulphuric acid or alkali.

Some information regarding the effect of temperature on the clarification of New Jersey water by means of alum is recorded by Velz (*Civil Eng.*, 1934, **4**, 345). " Floc " forms more rapidly at 8°–14° than between 14° and 24° C. Above 16° the optimum pH range lies below 5·8, but at lower temperatures a wider pH range prevails, so much so that good results were obtained up to pH 6·4.

Aluminium silicate has been used as a coagulant by Baylis (*J. Amer. Water Works Assoc.*, 1937, **29**, 1355), who employs aluminium sulphate together with sodium silicate in the ratio of 10 : 4 at pH 5·5–7·5. Under these conditions there is an appreciable increase in the silica content of the water.

From what has been written, it will be understood that pH control alone may be of comparatively little value, and will certainly provide no panacea for the troubles encountered in water treatment. If, however, it is carried out with a full knowledge of the contents of the water, then it constitutes a most valuable method of control. If a pH as low as 5·5 has been adopted, it is often found that the filtered water is corrosive, and that consequently its pH must be raised by means of sodium or calcium hydroxides.

The control of the pH of water is also of fundamental importance in conjunction with the use of bactericidal agents, probably owing to the redox potential, pH, and bactericidal efficiency being interdependent. Mallman (*Amer. J. Pub. Health*, 1933, **23**, 35, 269), investigating the disinfection of bath-waters, with residual chlorine at 0·2 p.p.m., found that bacteria of the *coli* type were all killed in 5 minutes at pH 6·0, 1 per cent. survived for 30 minutes at pH 7·0 and 44 per cent. survived for 30 minutes at pH 8·0. Similar observations were made by using chloramine-T. (See also Baars, *Zentral. ges. Hyg.*, 1934, **32**, 146). Johns (*Ind. Eng. Chem.*, 1934, **26**, 787) points out that the germicidal power of sodium hypochlorite is considerably retarded between pH 10·8 and 12·0.

The adjustment and control of the pH of water during treatment with chlorine, chlorine-ammonia mixtures, hypochlorites

and chloramine-T, are ● factors of considerable importance, especially in regard to the efficiency of sterilisation and the time in which it may be effected.

Chlorine and sodium hypochlorite are, in a given time, between twenty and thirty times as effective as the chloramines. According to Moore and Snow (*J. New England Water Wks. Assn.*, 1942, **56**, 320) the optimum *p*H for rapid sterilisation is about 6·5 ; the rate of sterilisation diminishing as the *p*H is increased.

When ammonia is used in conjunction with chlorine the latter should be injected into the water before the ammonia, and Griffin and Chamberlin (*ibid.*, 1941, **55**, 371) asserted the optimum *p*H range for plant operation is 6·5–8·5 with between 10 and 25 volumes of chlorine for one of ammonia. The velocity of the reaction :

$$NH_3 + HClO \rightarrow NH_2Cl + H_2O,$$
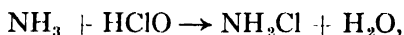
which is unimolecular with respect to both reactants, reaches a maximum value at *p*H 8·3. Moore (*Water and Sewage Wks.*, 1951, **98**, 130) found that, by using 0·8 p.p.m. of chlorine with 0·4 p.p.m. of ammonia in a water at *p*H 8·3 at 25° C., 99 per cent. of the chlorine was converted into chloramine in 1 minute whereas at *p*H 5 and *p*H 11, 210 minutes and 90 minutes respectively were required. Houghton (*J. Instn. Water Engrs.*, 1950, **4**, 434) found, by treating either bore-hole water or river water with 0·3 p.p.m. of ammonia and between 0·5 and 1·2 p.p.m. of chlorine at 18° C., that at *p*H 6·5 an appreciable amount of the chlorine remained as such after 15 seconds and even after several minutes, whereas at *p*H 7·5 the greater part had reacted in 15 seconds and at *p*H 8·5 almost all of the chlorine had combined.

Palin (*ibid.*, 1949, **3**, 100 ; 1950, **4**, 565) directed his investigation mainly towards the analytical control of the chlorination of water in regard particularly to the residual chlorine and the chloramine formed. With a chlorine : ammonia ratio of 5 : 1 at *p*H 7·5 the product was chloramine but as the ratio was increased there resulted an increasing loss of both chlorine and nitrogen. With large proportions of chlorine, a little NCl_3 and a trace of $NHCl_2$ were produced. Whereas under suitable conditions at *p*H 7·5 the loss of chlorine and ammonia may become almost complete, below *p*H 6·5 and above *p*H 8 an appreciable residuum of oxidation-products remain in the water. When albuminoid ammonia is present much longer time is required for its oxidation at *p*H 7·0–7·4.

Reference has already been made to the effect which algal

organisms have on natural waters during periods of profuse growth in raising the pH to 9·0 and even above. Occurring, as it does, in warm weather, the alkaline water becomes particularly corrosive to service pipes. Brockman (*Ind. Eng. Chem.*, 1933, **25**, 1402) has found that copper sulphate is a suitable algicide, and, moreover, that as long as the pH is maintained at 6·3 (basic copper sulphate is precipitated largely at this pH—see p. 70) a very heavy dose of copper sulphate may be administered without any risk of copper sulphate passing through the filters of a water filtration plant, especially where alum treatment is also being used. In a subsequent paper (*Water Works and Sewerage*, 1934, **81**, 275) he states that the floc formed with a ferric salt as coagulant is much more effective as a copper adsorbent than floc formed from an aluminium salt. Not only is the effective pH range wider, but smaller concentrations of a ferric salt will effect the complete removal of copper ions, even at pH 3·8, when, of course, aluminium sulphate is ineffective.

The pH value of water is important in regard to its sterility. There seems to be some grounds for the belief that bacteria of the colon and typhoid group are destroyed in media of pH greater than 9·5. A natural water which has been softened by treatment with the correct amount of lime to form calcium carbonate will have a pH value in the region of 9·5.

Ferrous sulphate is sometimes used in place of alum, but as will be seen from Fig. 121 on page 62 ferrous hydroxide, or, better, basic sulphate, is not completely precipitated until a pH of about 9 is reached. Its action, however, depends on the ease with which it undergoes oxidation to the ferric state by means of air, the rate of oxidation increasing with increasing pH, and then to precipitate as basic ferric sulphate. Hopkins and Whitmore (*Ind. Eng. Chem.*, 1930, **22**, 79) find that chlorine, used in conjunction with ferrous sulphate, provides an efficient coagulant which gives a compact easily settling floc at any pH above 3·5. Highly coloured swamp-water was considerably improved when lime was also added. A coagulant which apparently can be used in water of any pH value is " ferric alumina " (Moberg and Partridge, *ibid.*, 1930, **22**, 163).

The coagulant marketed in this country as " alumino-ferric " is largely aluminium sulphate, a little ferric sulphate being sometimes included. It is supplied in the form of blocks, around which the water, to be clarified, flows. By its gradual dissolution, it sets up a pH about 4 in its immediate proximity. It is extremely effective, especially with water in which highly dispersed clay or humus is suspended.

Ferric salts, sulphate and chloride, also serve as effective coagulants, especially in coloured waters. Their efficiency rests on the ease with which they hydrolyse to form fine colloidal suspensions of ferric hydroxide, which as the pH is increased coagulate as gelatinous flocs (see p. 90). Unfortunately, the very fine suspensions formed at low pH values do not coagulate and settle very readily. According to Bartow, Black and Sainsbury (*Ind. Eng. Chem.*, 1933, **25**, 898), their useful range as coagulants lies between pH 5·0 and 7·0, and it is therefore necessary to follow up the treatment with suitable amounts of alkali. Using ferric sulphate and sodium hydroxide, the zone of rapid floc formation is pH 6·0–6·5. The addition of sodium sulphate extends this zone to pH 5 or even to pH 4·0. Holton and Bean (*Water Works and Sewerage*, 1934, **81**, 229; see also Phillips, *ibid.*, 1943, **90**, 263) state that the optimum pH for colour removal with ferric sulphate is below pH 7, but they assert that lime treatment to pH 9·2–9·8 produces true ferric floc with complete removal of colour, residual iron and any manganese, whilst Hopkins (*Municipal Sanitation*, 1934, **5**, 85) claims that for most waters pH 5·5–7·2 is the range of effective coagulation with either ferric or aluminium flocculants, and that colour is best removed at about pH 4, although they admit that pH 8·3 is suitable in some cases. Francis (*Surveyor*, 1935, **88**, 33) advises the use of sodium aluminate with ferric salts.

Soluble aluminates, namely those of potassium and calcium, are finding application in water treatment (Barnett and Haux, *Can. Eng.*, 1926, **51**, 725, and Bardwell, *J. Western Soc. Eng.*, 1926, **31**, 392). Though the solutions themselves have pH values lying between pH 10 and 11, considerable quantities would have to be added to raise the pH of the water to 10, and so bring about the precipitation of magnesium hydroxide. Nevertheless, Bardwell has found that sodium aluminate does decompose magnesium salts present and reduces the scaly material to 1 to 1½ grains per gallon. Holmes and Fink (*Ind. Eng. Chem.*, 1929, **21**, 150) found that a mixture of calcium hydroxide and sodium aluminate imparted a pH of 10 or above, and was particularly useful as a coagulant in the chemical treatment of cannery wash waters. Snell (*ibid.*, p. 210) states that the addition of aluminium sulphate and slaked lime to impart to tannery effluents a pH of 7·6–7·8 brings about the precipitation of aluminium soap, fine dirt and albuminous matter. Fales (*ibid.*, p. 216) uses aluminium sulphate and adjusts the effluents from paper mills and tanneries to pH 5·2 before filtering through sand-beds.

Parker and Baylis (*J. Amer. Water Works Assoc.*, 1926, **15**, 22)

have devised a *p*H control apparatus,* using the tungsten elec-
trode, by which, not only can an automatic and continuous record
of the hydrogen-ion concentration of the treated water be obtained,
but also the addition of lime ,to bring the water to some desired
*p*H after filtration can be effected. Parker and Greer (*ibid.*, p. 602)
have designed apparatus for the *p*H control of boiler feed water
which they consider to be undoubtedly the cheapest method
available for its systematic control, and by which the chemical
dosage is not merely made proportional to the flow, but also
is made in such proportions as to compensate roughly for the
acidity, the amount of scale being formed and the corrosive
salts present.

The removal of fluoride from drinking water can be effected
with aluminium sulphate, but Boruff (*Ind. Eng. Chem.*, 1934, **26,**
69) and Upton and Buswell (*ibid.*, 1937, **29,** 370) have also tried
titanic sulphate. It was not superior to aluminium sulphate,
although it had a wider effective *p*H range. A mixture of ferric and
titanic sulphates, prepared from ilmenite, gave much better co-
agulation from coloured water, which was high in colloidal matter
and dissolved salts, than did either aluminium or ferric sulphates.

Corrosion.

The treatment of water such that it may have the minimum
corrosive action on the metal surfaces with which it comes into
contact is of paramount importance. This difficulty arises not
only in connexion with service pipes but also with boilers and
heating systems.

Among the factors involved in the process of corrosion of a
metal are the following : (1) the normal electrode potential of the
metal and its hydrogen overvoltage, and the manner in which these
are influenced by the impurities present in the metal ; (2) the
hydrogen-ion concentration of the water ; (3) whether there are
any metals in electrical contact with the metal, and if so, their
electrochemical nature ; (4) the oxygen and salt contents of the
water ; (5) the ease with which any hydrogen liberated at the
metal surface is removed, especially by any possible catalytic
oxidation, by the dissolved oxygen or other oxidising agents ;
(6) the presence of possible passivating agents ; and (7) the
pervious nature of the oxide film to oxidising agents.

We shall concern ourselves here only with the influence which
the hydrogen-ion concentration of water may have on the cor-
rosion of iron. Since acids have a solvent action on iron, their
corrosive action may be represented by the reaction

$$Fe + 2H^{\cdot} \rightleftharpoons Fe^{\cdot\cdot} + H_2.$$
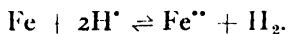
The direction taken by this reaction will be determined by the pH of the water, and the electrode potential of iron together with its hydrogen overvoltage. The continued reaction towards the right will be determined by the ease with which the hydrogen gas film can be removed from the surface, either mechanically or by oxidation. Furthermore, this will depend upon the nature of any oxide or, better, hydrated oxide film which may have been deposited on the surface. Such a film may have a distinct protective action. The formation of the film depends upon the concentration of ferrous ions which has been produced, and whether this and the hydroxyl-ion concentration of the water will be sufficient to exceed the solubility product of ferrous hydroxide. Once this film has been formed at the metal surface, its character will depend upon its subsequent oxidation to the less soluble ferric hydroxide.

Sweeney (*Trans. Amer. Electrochem. Soc.*, 1928, **53**, 317) has calculated from thermodynamic considerations that even in the absence of oxygen there is a small driving force tending toward the formation of ferrous hydroxide and hydrogen according to the equation :

$$Fe + 2H_2O \rightarrow Fe(OH)_2 + H_2 \text{ (1 atmos.).}$$

Once this reaction has proceeded to an extent that the solubility product of ferrous hydroxide becomes exceeded, then the magnitude of the driving force (*i.e.*, the capacity of the reaction of doing external work) should be independent of pH of the solution with which the iron is in contact. The rate of corrosion, however, will depend, among other things, on the pH, the hydrogen overvoltage, diffusion through the surface film, and catalytic effects. Using Britton's data concerning the precipitation of ferrous hydroxide, he has obtained a curve connecting the pH of solutions with the concentrations of iron dissolved, which is in remarkable agreement with the solubility of iron in natural waters of differing pH values as found by Baylis (*Ind. Eng. Chem.*, 1926, **18**, 370).

Wilson (*Ind. Eng. Chem.*, 1923, **15**, 127) found that iron underwent rapid corrosion when immersed in solutions of pH less than 4·3. Here the hydrogen overvoltage was the controlling factor, and the effect of the dissolved oxygen was negligible. When iron was immersed in an acid solution of pH greater than 4·5 appreciable amounts of hydrogen were formed, first as dissolved gas, but in solutions of about pH 4 bubbles of hydrogen became perceptible. When iron is placed in contact with other metals of low hydrogen overvoltage, this gas evolution may often begin

in solutions of higher pH, but it must be remembered that the hydrogen-ion concentration still remains one of the controlling influences. At pH values higher than 4·3 iron becomes covered with a protective coating. The extent of the protection afforded is again largely a question of pH. From about pH 5 to about pH 10·5 this layer permits the passage of dissolved oxygen through it, thereby enabling corrosion to take place, though at a somewhat reduced rate. In the more alkaline solutions the hydrogen produced at the surface becomes negligible, though the effect of oxygen on the film becomes more marked. This yields a more resistant coating, and as a consequence corrosion becomes further reduced. Thus it follows that as far as actual corrosion is concerned, the amount of dissolved oxygen removed from water may be regarded as a measure of the extent of corrosion in any given time. Whitman, Russell and Altieri (*ibid.*, 1924, **16**, 665) found that the equation : $3O_2 + 4Fe \rightarrow 2Fe_2O_3$ represented the reaction to the extent of about 95 per cent. They therefore carried out experiments in which oxygen-laden water, adjusted to various pH values by means of either hydrochloric acid or sodium hydroxide, was allowed to flow at a uniform rate, about 2·2 litres per minute, through a steel box having baffle plates with a total surface of 17,400 sq. cm. From determinations of the oxygen contents of the influent and effluent waters, the amounts removed through corrosion in a given time could be ascertained. Fig. 183, showing the amounts of oxygen removed from each litre of water at different pH values, indicates the influence of temperature in accelerating corrosion, and also that the corrosive attack was considerable in acid solutions below pH 5. Between pH 5 and 9 the extent to which corrosion took place was not greatly affected by the hydrogen-ion concentration, except that it was not entirely prevented. Above pH 9 the effect of enhanced alkalinity becomes evident in rendering the rust film more protective. Similar conclusions have been arrived at by Shipley and McHaffie (*Can. Chem. Met.*, 1924, **8**, 121), who found that corrosion of iron in the absence of oxygen is proportional to the hydrogen-ion concentration up to pH 9·4, at which point the evolution of hydrogen gas almost ceases.

Rogers (*Ind. Eng. Chem.*, 1938, **30**, 1181) has observed that steel pipe lines, buried in Kalmia sand, corrode at less than half the rate at pH 9·75 than at pH 4·5.

A method of estimating the relative corrosive action of different soils on iron due to Holler (*J. Washington Acad. Sci.*, 1929, **19**, 371 ; *Ind. Eng. Chem.*, 1929, **21**, 750), consists in measuring the rate at which hydrogen is evolved when equal

weights of soil and either steel turnings or pulverised cast iron
are allowed to interact in the presence of water.   The volume
of hydrogen appears to depend on the pH value and the extent
to which the pH value can be maintained by the buffer salts
present.   The corrodibility of iron by a soil therefore bears a
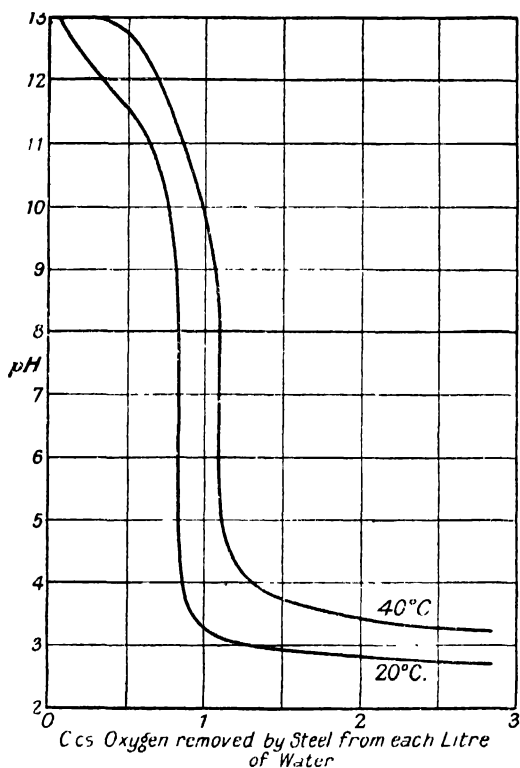
FIG. 183.—Corrosion of Steel by Oxygenated Water.

direct relation to the soil acidity, which Holler finds by titrating
a 5 per cent. potassium chloride solution soil extract to pH 9·4,
which is regarded as the point at which iron ceases to corrode
when oxygen is excluded.

Hydrogen-ion concentration is also an important factor in the
corrosion of other metals.   For instance, water of too low a pH
value, such as may be produced by the addition of too much alum,
or has been obtained from swampy areas where it has become
contaminated with decomposing organic matter, will be particu-

larly corrosive to lead, zinc and aluminium.   Such water when
conveyed through lead pipes may lead to lead-poisoning.   Pro-
tective coatings of hydroxide or basic carbonate are usually formed
on metals in contact with waters of high pH.   In cases of metals
capable of forming amphoteric hydroxides, *e.g.*, aluminium and
zinc, corrosion also is set up by waters of high pH.   With
galvanised vessels and pipes corrosive action is at a minimum at
pH 9·5 to 10.

Both phosphates and chromates are employed as corrosion

TABLE 222

pH OF WATER AND NaCl-SOLUTIONS AFTER CONTACT FOR
400 HOURS WITH VARIOUS METALS

Initial pH: 6·9–7·0

Metal.	Distilled Water.	pH of 6 per cent. NaCl Solution.	20 per cent. NaCl Solution.
Mg	9·9	12·4	12·2
Cd	7·8	8·8	9·4
Zn	7·4	9·8	8·4
Fe	7·5	6·8	6·7
Al	6·9	7·1	7·1
Duralumin . .	6·9	6·8	6·9
Ni	7·3	8·8	8·8
Cu	6·7	8·8	8·7
Brass	7·2	8·2	8·7

inhibitors, but Kahler and Gaughan (*Ind. Eng. Chem.*, 1952, **44**,
1770) claim that when used together in suitable concentrations
in the water of cooling systems with the water controlled at
pH 6·0–6·3 a much greater resistance to corrosion is provided
than can be obtained from the use of either separately.

Light metals and alloys being less noble than iron are more
readily corroded by sea-water, oxygenated water and alkaline
solutions.   Scheifele (*Paint, Var. Prod. Mfr.*, 1938, **18**, 220 ;
Farben-Ztg., 1936, **41**, 1063) points out that any water entrapped
in films of paint covering such metals may promote corrosion.
Rossmann, Hang and Kiebitz (*Fette u. Seifen*, 1938, **45**, 503) have
measured the pH of the water-leachings of paint-films.   The pH
of old linseed oil films ranged from 2·6 to 3·4.   Zinc oxide raised
the pH of linseed oil, films of which after weathering for three
months gave leachings of pH 8·8 as compared with pH 5·5
initially.   Red lead paint deposits increased from pH 5·5 to 6·3.
The neutralising action of these pigments materially assists the

paints in which they are embodied to reduce corrosion of the basis metal.

Another important factor is the pH set up by the metal itself when brought into contact with water, and especially with sea-water. Whitmore (*Ind. Eng. Chem.*, 1933, **25**, 23) has found that the pH of water and salt-solutions when kept in contact with the metals given in Table 222 changes in many cases towards alkalinity in the sodium chloride solutions.

Below pH 3 magnesium is rapidly corroded, but between pH 3 and pH 7 the rate of corrosion rapidly decreases, whilst at pH 11 a protective film is formed and the rate of corrosion falls abruptly (Akimov and Rosenfeld, *Compt. Rend. Acad. Sci.*, U.S.S.R., 1944, **44**, 193).

Sewage Disposal.

The chief processes involved in the activated-sludge method of sewage disposal are (1) digestion and (2) further precipitation of solid matter, and facilitating filtration. In both these processes control of hydrogen-ion concentration has been found to be of great service.

In the digestion process, the so-called " activated sludge " is produced. It consists of flocs due to microbial growth, which has been assisted and accelerated by aeration of the sewage. This sludge, after being allowed to settle, is separated by decantation from the liquor which is mixed with fresh sewage and again subjected to air treatment. In this process, some of the matter is oxidised and passes away as carbon dioxide, whereas under certain conditions bacterial action promotes reduction, resulting in the evolution mainly of methane, though occasionally higher hydrocarbons and hydrogen are formed. As a result of these complicated reactions, humus together with other organic matter are precipitated. Sometimes it is desired to give badly digested sludge a further bacterial treatment, so as to bring about a separation of colloidal matter from the liquor. Incidentally, where it is desired to dry the sludge for use as manure it is found that the insoluble matter deposited in the aeration tanks is too much swollen through the imbibition of water. The water-content can be reduced by the same treatment accorded to poorly digested sludge.

Considerable attention has been given by Rudolfs (*New Jersey Agr. Exp. Station, Bull.* No. 427), and Fair and Carlson (*Eng. News Record*, 1927, **99**, 881) to the pH changes which occur during digestion. The digestion of properly seeded sewage solids, as measured by the rate of gas evolution, normally takes place in

three stages : (1) the " acid " stage, (2) a long period of very slow digestion, and (3) the " alkaline " stage, in which methane is produced. During each of these stages the measurement of pH provides an excellent guide of the extent to which digestion has proceeded. (See, however, Clark and Adams, *Ind. Eng. Chem.*, 1929, **21**, 258.)

The liquor in contact with freshly settled sludge from ordinary sewage has a pH of about 7. After standing for a few hours, the separated sludge begins to show signs of bacterial decomposition, in the form of gas evolution and the milky appearance of the liquid. The pH value falls to about 5, and, besides the development of a foul odour, the sludge becomes sticky and slimy and difficult to drain. Such a pH value, being very near to pH 4·7, the isoelectric point of many ampholytic bodies, is not conducive to the passage into solution of nitrogenous bodies. This concentration of hydrogen ions has an inhibiting action on the process of digestion which is characterised by a low gas production, and a slowly increasing pH value. Under normal conditions this phase of the process requires about six months. Fair and Carlson investigated the effects produced by adjusting the pH values to 6·8, 7·2, and 7·6 by the addition of lime, marble dust or dolomite dust. In all cases the length of this period was considerably shortened and gasification was greatly accelerated. By adopting pH control the time necessary was reduced to about eight weeks. Their experiments showed that the optimum pH in the control of sludge digestions varies according to the stage of digestion reached by the decomposing matter. It would appear that a pH of about 6·8 is the optimum during the initial stage while pH 7·2 should be afterwards obtained.

In the third stage of an uncontrolled digestion, the pH rises to about 6·8 and methane production becomes active, whilst the sludge becomes non-putrid, does not foam (*cf.* Hatfield, *Ind. Eng. Chem.*, 1930, **22**, 172) and possesses a slight earthy or tarry odour.

The formation of sludge is especially sensitive to changes in hydrogen-ion concentration. At ordinary temperature, the optimum pH is 7·4 (Cramer and Wilson, *Ind. Eng. Chem.*, 1928, **20**, 4). The pH's of liquors are maintained by the addition of lime and by having an excess of digested sludge over the fresh solids present. Parker (*Ind. Eng. Chem.*, 1927, **19**, 660) describes an automatic pH control, by means of the tungsten electrode (see page 302), which has been installed at Winston-Salem, and by which the addition of the requisite amounts of milk of lime is manipulated and regulated. Values of pH ranging from 6·8

to 7·8 appear to be used•for sewage digestion by operators of thirty different plants (Bachmann, *Sewage Works J.*, 1929, **1,** 218). Keefer and Kratz (*Eng. News Record*, 1929, **102,** 103) state that pH 6·8 favours gasification, though pH 7·2 leads both to gas production and liquefaction of the sludge. In regard to the possible drying of sludge on beds it must be remembered that at pH 6·4 and pH 8·4 the odours are particularly disagreeable, the former being of sulphuretted hydrogen and the latter similar to that of rotting fish. Rudolfs (Rudolfs and Zellar, *Pub. Works*, 1927, 253; Rudolfs and Henkelekian, *N.J. Exp. Stn.*, 1929; *Pub. Works*, 1927, 2, 50) apparently does not find that high pH values lead to diminished gasification. Milk of lime is generally advocated as being the most suitable agent for the adjustment of the pH value, and Clark and Adams (*Ind. Eng. Chem.*, 1929, **21,** 258) have found that calcium carbonate is unsuitable owing to its slight solubility.

According · to the Annual Report of the Water Polution Research Board (*H.M.S.O.*, 1934) the maximum rate of air—oxidation of sewage and biologically active sludge occurs between pH 6·6 and pH 9·0. Below pH 6·6, the rate decreases with pH, until at pH 5·0 no appreciable oxidation takes place in 9 hours. Ammonium salts in sewage oxidise between pH 8·0 and pH 9·2. Dawson and Jenkins (*Sewage Works J.*, 1949, **21,** 643) found that it is the solid portion of activated sludge which is responsible for the uptake of oxygen, for which the optimum pH range is 7 to 8.

Sewage containing phenols, *e.g.*, from tar works, can, according to Kufferath (*Z. angew Chem.*, 1929, **42,** 65), be treated by the activated sludge process if selected micro-organisms are added and the pH set at 7·2.

In anaerobic sludge digestion nearly all the odour is caused by hydrogen sulphide. Hammond and Copeland (*Proc. Amer. Soc. Civ. Eng.*, 1929, **55,** (1), 599) state that this smell can be prevented by keeping the pH of the sludge at 7·3–7·6 by means of slaked lime. Liquefaction of the solids occurs more freely between pH 6·8–7·2, and gasification between pH 7·5–7·8. Control is necessary during the initial fermentative stage, for the carbon dioxide and fatty acids formed may reduce the pH to as low as 5·5 (see also Neave and Buswell, *Ind. Eng. Chem.*, 1928, **20,** 1368). The use of ferric salts as coagulants, through the formation of sulphides, reduces odour. In places where the sewage has to be carried long distances, the odour can be reduced by adding lime sufficient to maintain the sewage at pH 7·2–8·5. II. Wilson (*J. Roy. San. Inst.*, 1935, **55,** 335; *Surveyor*, 1935,

87, 223) recommends that the lime should be added at a point one and a quarter miles above the outfall works.

Due to the fact that the density of sludge formed in the region of pH 7·3 is greater than that of water, through its enhanced absorption of water, the sludge sinks, and this also occurs when the sludge has not undergone complete digestion. The slimy nature of the latter renders extremely difficult the separation of the liquors, which on account of the poor digestion still contain appreciable quantities of putrefying matter. If the pH value is brought to pH 3 to 5, it is found that not only does the badly digested sludge float but that the coagulation of a considerable amount of the organic matter occurs, with the result that efficient filtration is greatly facilitated.

Wilson (*J. Soc. Leather Tr. Chem.*, 1921, **5**, 268) has applied the Procter-Wilson theory of the swelling of jellies to the filtration of activated sludge at Milwaukee. The rate of filtration was shown to be a function of the pH and was increased three-fold by adjustment to an optimum pH of 3·2. By using aluminium sulphate, however, and bringing the pH to 4·3 the rate of filtration was increased seven times. Slightly higher efficiencies are reported by Cramer and Wilson (*loc. cit.*). They further point out that the filtering efficiency of aluminium sulphate sludge adjusted to pH 4·4 increases from 7·5 to 40 times when heated to 80° C. It is interesting to find that the optimum for aluminium sludge is pH 4·4, which is, as shown on p. 76, approximately the point at which basic aluminium sulphate undergoes precipitation. It is probable that the coagulating and filtering efficiency is due to the buffer action of basic aluminium sulphate during precipitation thereby enabling a pH to be established quite near to the isoelectric point of most organic bodies. The action seems to be identical with the tanning action of basic aluminium sulphate, which, in effect, is probably nothing more than the mutual precipitation of two colloids. After coagulation with ferric sulphate and chloride, Edmondson and Lumb (*J. Inst. Sewage Purif.*, 1934, **1**, 83) find that the optimum pH for vacuum filtration is 3·0.

When filtration becomes more difficult through low temperature in winter-time, Cramer and Wilson found that the adjustment of the pH of the sludge to what they regard as its isoelectric point, namely pH 3·4, with ferric chloride, instead of sulphuric acid, results in an increase in filtering efficiency of thirty times the normal rate. Such an increase makes the operation of the plant possible. At Milwaukee more than a million gallons of sludge, drawn from over 85 million gallons of sewage, are so treated per

day. This sludge is converted into excellent dry fertiliser to the extent of 100 tons per day.

Donaldson (*Water Works and Sewerage*, 1934, **81**, 139) finds that ferric chloride brings about coagulation from mixed sludge (at pH 6·0) at pH 4·2. The coagulum contains 5·5 per cent. of sewage solids. Treatment with milk of lime to pH 11·5 gives a better coagulation, the coagulum containing 9·4 per cent. of sewage solids. Rudolfs and Gehm (*Sewage Works J.*, 1936, **8**, 442), however, find that good clarifications are possible at pH 2·5–3·5 and at pH 9·5–10·5, whilst Eldridge and Theroux (*Michigan Eng. Exp. Stat.*, 1934, *Bull.* 55, 3) state that with ferric chloride the coagulation range is generally pH 6·5–8·0. Much suspended matter may, however, be removed at lower pH values. Potassium permanganate used in conjunction with ferric chloride raises the pH at which coagulation occurs.

The mechanism of coagulation and flocculation of sewage colloids can best be explained, according to Lumb (*J. Inst. Sewage Purif.*, 1933, **1**, 79), on the basis of Baly's Theory of the Activated Sludge Process (*Trans. Faraday Soc.*, 1931, **27**, 193 ; *J. Soc. Chem. Ind.*, 1931, **50**, 23T). Baly states that the apparent isoelectric point of sewage colloids in the presence of 0·17 per cent. NaCl (the amount of salt normally found in sewage) is at pH 6·5. With 3 per cent. NaCl, the isoelectric point is raised to pH 8·3, whilst by diluting sewage with 15 times its volume of distilled water the isoelectric point falls to pH 4·6, a value in common with that of many proteins. He considers that above pH 6·5 both the sewage colloids and the active bacteria are electro-negatively charged, and electro-positively below pH 6·5. As the pH of ordinary sewage is 7·4, both the bacteria and sewage colloids carry a negative charge. The charge carried by the bacteria is believed to be relatively greater than that carried by the sewage colloids and consequently that, owing to the tendency for the free energy of the system to decrease, co-precipitation should result. Baly suggests that the success of the activated sludge process is to be attributed to the enhanced charge on the bacteria when in their state of maximum activity. The process should therefore be operated at pH 5·8–6·0. Lumb obtained most satisfactory coagulations and flocculations by adjusting the sewage to pH 6·5 by adding sulphuric acid before the bio-aeration process. (See also Mills, *J. Soc. Chem. Ind.*, 1932, **51**, 374T.)

Similar considerations apply to the disposal of industrial, wastes, *e.g.*, the effluents from tanneries, textile-mills, creameries especially in regard to the efficiency of the various coagulants used.

CHAPTER XLIV

THE BEARING OF HYDROGEN-ION CONCENTRATION ON THE FERTILITY OF SOILS

pH and Soil Chemistry.

THE extensive application, during recent years, of the principles of pure science to the study of the complex phenomena involved in soil management and cropping has emphasised the importance of the hydrogen-ion concentration of the soil as a factor in its fertility. The recognition of " sourness " in soils and of the common remedial measures of liming, chalking, or marling doubtless dates back to the earliest days of systematic husbandry. The less extreme variations in soil reaction and the accompanying less obvious effects on crop yield have been the subject of scientific inquiry only in very recent years. Definite attempts to correlate soil " sourness " with the presence of acids have, however, merely served to emphasise the wide scope and complexity of the general problem. In a few extreme cases it has been recorded that soils have indicated the presence of acid substances directly by the reddening of moist blue litmus paper, but by far the greater number of soils which to the practised eye of the agriculturist are sour fail to demonstrate their acidity in so simple a manner. The relatively enormous volume of recent research work, whilst throwing much light on the chemical processes concerned in the souring of soils, has not yet brought either a clear conception of the numerous contributing causes or the *modus operandi* of their manifold effects.

The recognition of the extreme sensitiveness of the majority of living organisms to changes in the alkalinity or acidity of the media in which they live and from which they obtain their food materials, has profoundly affected our conception of the mechanism of plant growth. Changes in the hydrogen-ion concentration in the soil not only affect the plant directly, but also modify both the physical and chemical conditions of the soil and the distribution and activity of its teeming population of micro-organisms. Each of these latter factors in turn may indirectly affect the nutrition of the plant. We will now consider more fully some of the effects above mentioned.

Hydrogen-Ion Concentration and Plant Growth.

Detailed study of the nutrition of a number of plants has shown a very close relationship between crop yield and the hydrogen-ion concentration of the nutrient solution. Generally speaking, there is not only a definite range of pH values outside of which the plant will not grow at all, but also, within the range of possible growth, a much narrower range corresponding to the region of optimum growth. The work of O. Arrhenius shows that graphical representations of the relationship between crop yield and the reaction of the nutrient media are of the form illustrated in Fig. 184.

$\longrightarrow$ *pH*
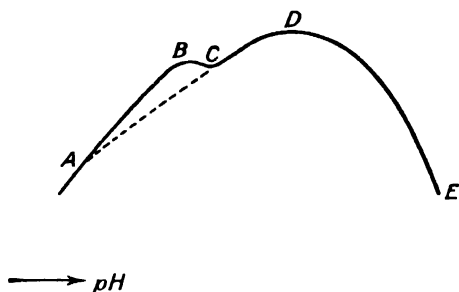
FIG. 184.—*p*H of Soils and Yield of Crops.

The characteristics of these growth curves are—

(1) A fairly wide range of *possible* growth.
(2) A relatively narrow range of optimum growth.
(3) A more rapid falling-off of crop yield on the alkaline side of the optimum, *i.e.*, a steeper curve, than on the acid side.
(4) In many cases a secondary maximum in the curve, *i.e.*, the portion ABC, lower than the principal optimum CDE.

The extreme range of pH values in ordinary soils is from pH 3·5 to 8·0. Few, if any, plants can grow outside this range, and very few can withstand the conditions obtaining in the whole range of pH values within these limits. The work of Olsen (*Compt. rend. Lab. Carlsberg*, 1923) indicates that the growth range of individual species of plants is generally restricted to 3·5 units of pH, with optimum conditions over ranges of 0·5 to 1·5 units. Naturally the majority of our existent species of plants have an optimum range of pH 6·5 to 7, this being a mean value in our arable soils. Typical acid-loving plants have an optimum range

at pH 4·5 to 5, and at values approaching the neutral point become stunted and chlorotic.   Plants that flourish in neutral soil seldom thrive at pH values greater than 7·3 to 7·4, and from pH 7·5 upwards growth is more or less restricted to aquatic or semi-aquatic plants.

The following table shows pH values of the growth ranges and optimum ranges for a number of common agricultural crops grown under artificial nutrient conditions, that is, under conditions in which adequate nutrient material is supplied throughout and only the actual pH values are allowed to vary :—

TABLE 223

OPTIMUM pH RANGE FOR GROWTH OF COMMON CROPS

Crop.	Growth Range pH.	Opt Range pH	General Remarks.
Potato	—	5·0–5·5	Uninjured at 4·2
Barley	6·5–8·0	6 6	—
Oats	—	4·5–5·8	Injured at 4·3
Wheat	5·2–7·0	—	—
Rye	4·2–7·6	6·2	.—
Turnips	5·0–6·5	6·0–6·5	– –
Lucerne	6·0–7·2	7 0	—
Sugar beet	—	7·0 · 7·2	—
Pasture grasses (average)	5·0–6·5	6·0	-
Sugar cane	—	7·0	. —
Tea	—	5·4	—
Rice	—	7·9	—
Tobacco	4·5–6·0	5·6	—

It is interesting to observe that even among these agricultural crops selected over generations to suit soils not varying greatly from the neutral point still show a considerable variation in the optimum growth ranges.

The distribution of pasture plants and grasses in relation to soil pH has been investigated by Atkins and Fenton (*Sci. Proc. Roy. Dublin Soc.*, 1930, **19**, 533), who record the pH ranges for the growth of numerous species.   They have observed that sheep and cows when allowed to roam freely graze closely on herbage growing in soil at pH 6·5, and will not graze off most sites whose pH is less than 5.   They claim that to all intents grazing ceases at pH 5.

A further point of interest, not apparent in the above figures, is that although the optimum ranges of pH for a number of plants may be similar it does not follow that the growth ranges are similar

or that injury is observed in soils of similar pH.   Thus Olsen has recorded that the optimum ranges for three typical crops are—

Lucerne	6·5–7·0
Rye . . . . , . .	6·0–6·5
Buckwheat . . . , . .	6·0–6·7

yet at pH 4·0 the crop yields of these three plants expressed as percentages of the respective optimum yields are—

Lucerne	13	per cent.
Rye	82	,, ,,
Buckwheat	90	,, ,,

The figures quoted above relate to plants grown under strictly controlled laboratory conditions, in which the only variant is the pH value of the nutrient medium.   When we come to examine plants growing under natural conditions in soil the effects of variations of reaction are less easy to trace.   The solubility or availability of the mineral nutrients of the soil are marked by, or influenced by, changes in the pH value, and the direct effect of the latter on plant growth becomes merged into the effect of changes of nutrition.   As a result, the apparent optimum pH range for a particular plant growing in one locality may differ considerably from that of the same plant growing elsewhere.   Moreover, the effects of differences in temperature, amount and rate of water supply to the plant roots, hours of sunshine, together with other climatic and regional conditions become operative.   Under natural conditions, therefore, the relationship between soil reaction and plant growth becomes to some extent specific to local conditions.   This point becomes of considerable importance in evaluating the lime requirement of soils (see later).   The effect of local conditions on the apparent optimum pH range on plant growth for a number of farm crops is well illustrated by von Kreyberg.   Table 224 shows the apparent optima in (1) a humid climate, (2) a moist climate and light sandy soil.

TABLE 224

OPTIMUM pH RANGES FOR PLANT GROWTH IN DIFFERENT CLIMATES

Crop.	Soil (1)	Soil (2).
Wheat	7·3–7·8	6·4–6·9
Barley	7·6–8·2	6·2–6·9
	4·1–6·5	
Sugar beet . . .	7·6–8·5	6·6–7·3
Red clover	8·3–8·7	6·0–6·8

The inter-relationship between plant growth and soil reaction, coupled with the fact that the optimum ranges of pH for the growth of plants varies with the species, is the primary basis of certain peculiarities in plant distribution long recognised by the practical agriculturist as indications of sourness in soils. There is, of course, no sharp line of demarcation between the natural herbage of soils of different reaction value. Nevertheless a relatively small change of, for example, 1 to 2 units of pH value is sufficient to retard the growth of certain types of plants and to encourage others to a corresponding extent, and the relative proportions and fullness of growth of certain plants frequently furnish information to a close observer as to the degree of " sourness " obtaining in a particular soil.

Among the " tell-tale " weeds of sour soils are spurrey, sheep's sorrel, sourdock, bedstraw, and bracken. Spurrey is a fairly sensitive plant to reaction changes, but the distribution of the remainder is fairly general. There is, however, a notable increase in the numbers and size of fundamental plants on acid soils, which makes these species of value in indicating acid conditions. More important than any of these, in connexion with sour soil indicators, is clover, and in particular the wild white clover. In this case, soil acidity is marked by the complete absence of the plant among the natural herbage. It would seem, however, that even in sour soils, seed or rootstocks remain dormant for lengthy periods, for in the majority of cases treatment of sour soils with lime or more generally with basic slag results in the appearance of a considerable yield of white clover in the ensuing season. The value of clover and of leguminous plants generally in the nutrition of animals renders their presence in herbage a matter of very great importance. As a result, much of the economic interest in the reaction of meadow land and pasture has centred round its effects on the growth of clover.

Speyer and Eberle (*Arb. Biol. Reichsanst. Land. Forstw.*, 1928, **16,** 325) stated that one of the few weeds to be found only on soils below pH 5·7 was the Annual Knawel (*Scleranthus annus*).

Pipe draining appears to reduce the sourness of soils, for, according to Thomas and Elliot (*J. Soc. Chem. Ind.*, 1931, **50,** 349T), it increases the mean of a soil to a depth of 30 inches.

Soil Micro-organisms and Hydrogen-Ion Concentration.

Even more sensitive than plants to changes in soil reaction are the soil bacteria, and among these none are more necessary to plant growth than the various species concerned in what is usually described as the " Nitrogen Cycle," *viz.*, that continuous suc-

cession of processes in which nitrogen becomes in turn a nutritive substance of plant, animal, and soil organism. Generally speaking, acidity tends to retard the activity of soil bacteria, which, although capable of existence and even of slight activity over nearly the whole range of normal pH valûes in soil, have a range of optimum activity narrower than that of plants. The growing
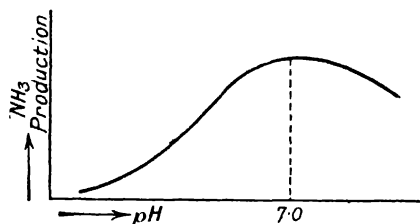
FIG. 185.

plant usually absorbs its nitrogenous food material in the form of nitrate and the transformation of the protein matter of animal and vegetable waste to nitrate is entirely a biological function, and depends on the activities of a succession of organisms each concerned in one of the usually accepted stages of transformation of organic nitrogen → ammonia → nitrite → nitrate.
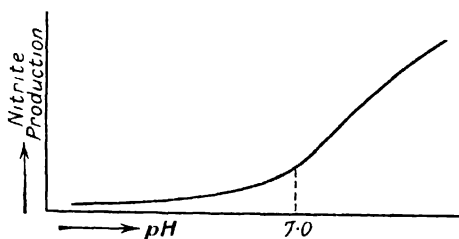
FIG. 186.

The various organisms involved in these changes are differently affected by changes in soil reaction. Figs. 185 and 186 are typical representations of the relationships between pH values of soil and the activity of (a) organisms such as *B. Mycoides*, *B. Fluorescens*, *B. Caudatus*, and probably some fungi which bring about the transformation of organic nitrogen compounds to ammonia, and (b) those such as *B. Nitrosomonas*, converting ammonia to nitrate, and *Nitrobacter*, responsible for the major transformation to nitrate.

It is to be observed that in the neighbourhood of the neutral point the ammonifying organisms have optimum activity, whilst the nitrate producers have not yet reached optimum productivity. Nevertheless the rate of conversion of ammonia to nitrate is so much greater than the preceding change that in normal soils little or no ammonia is found. A small change of pH toward the acid zone results in a relatively small decrease in ammonia production, but a very substantial reduction in nitrate formation, with the result that under milder acid conditions there is a tendency for ammonia to accumulate. Moreover, since ammonia is not available as a nutrient to most plants, we have here an illustration of one of the several indirect ways in which acidity in field soils tends to retard the growth of plants. Direct observation shows that in soils of pH greater than 6·5 nitrification proceeds more rapidly than ammonification. In the region of pH 6·5 to 6·0 the rate of the two processes approach each other closely. In most soils at pH 5·5 there is a distinct accumulation of ammonia, and in the region of pH 4·5 nitrification has practically ceased. The ammonifying organisms are, however, still active though at a somewhat reduced rate and even at pH 3·5 are able to carry out their particular function.

Perhaps the most sensitive among the organisms of the nitrogen cycle are those capable of fixing the free nitrogen of the atmosphere, *viz.*, the several species of *Azotobacter* and the *Clostridium Pasteurianum*. Gainey showed among a great number of soils examined by him, that those having pH values less than 6·0 were invariably free from nitrogen-fixing organisms, whereas all soils more alkaline than pH 6 contained these organisms.

Inoculation of the more acid soils with cultures of the organisms failed. Fixation of nitrogen proceeds but slowly in soils of pH 6·0 to 6·8. From 6·8 to 7·0 there is a sharp acceleration in the activities of these bacteria and an optimum condition exists at about pH 7·1 to 7·2. So remarkable is the rapid increase in nitrogen fixation with change of pH from acid conditions to the neutral point that it has been suggested that the nitrogen-fixing organisms might well be utilised as indicators in the determination of the lime requirement of soils (*i.e.*, the amount of lime necessary to eliminate "sourness" in soils). Although this process has not been generally adopted, it nevertheless provides information of practical value, and, as a biological test, finds favour among some investigators as being independent of any theory of the chemical nature of soil acidity.

Still another class of bacteria concerned in the nitrogen cycle are those species of organisms capable of reducing nitrites and

nitrates in soil, the nitrogen of which very largely reappears as the free element. Fortunately these organisms are of less significance in arable soils, but under certain conditions, *e.g.*, in water-logged soils where soil aeration is impossible, the denitrifying organisms may become active. A number of species is involved, but generally speaking they may be classified according as they utilise nitrites or nitrates in their metabolic processes. The former class has been less thoroughly examined, but it is established that they are most active in mildly acid soils, having an optimum range of pH of 5·5 to 7·0. Their activity ceases at about pH 7·3. but on the acid side of the optimum the range seems more extended. The second class of organisms is differentiated by being more favoured by alkaline conditions. The optimum range is pH 7·0 to 8·1 ; at pH 6·1 to 6·4 their activity becomes very low and at pH 5·5 on the one side and pH 9·8 on the other reduction of nitrates ceases altogether. The difference in reaction ranges of these two types of reducing bacteria serves to explain the accumulation of nitrates in certain waterlogged soils and not in others.

If the pasture on acid land is examined closely it will frequently be found that, instead of a firm soil surface immediately beneath the growing grass, there is a matted layer of half-decayed grass stems —the accumulation of, perhaps, many years. In sweet soils these grass residues rot down and become an intimate part of the soil. This is the result of certain classes of cellulose-destroying organisms which convert the tissues of the grass into the dark spongy " humus " characteristic of the appearance of a well-rotted manure heap. Examination of the top soil of a healthy pasture shows it to be considerably darker in colour than the subsoil, due to the steady accumulation of humus matter. The organisms bringing about the decomposition of cellulose have an optimum range of activity of pII 6·8 to 7·5 and are sharply affected by slight acidity, becoming almost inactive at pH 6·0 to 6·5. The result of their inactivity is manifest in the " mat " of grass residues characteristic of acid pasture. In practice this " mat " can never be satisfactorily cleared until the cellulose-splitting organisms can be stimulated into activity by suitable adjustment of the soil reaction. The preparation of " artificial farmyard manure," which in recent years has closely followed the work of Hutchinson and Richards at Rothamsted, affords yet another example of the importance of regulating the reaction of the medium in order to maintain the vitality of the cellulose-splitting bacteria. The process is essentially a large scale representation of what happens in the surface soil of pastures. The nitrogen which these organisms need is

supplied artificially, but unless the reaction of the fermenting mass of cellulosic material is maintained neutral or slightly alkaline the process of cellulose conversion becomes slow or practically ceases, the stack does not " heat " sufficiently and the product is of a very inferior quality.

According to Bennett (*Soil Sci.*, 1943, **55**, 427) purified lignin (from maize cobs) has many of the properties of humus, *viz.*, base exchange and buffer action particularly in the range, pH 4·5–6·5, but Perrenoud (*Mitt. Lebensm. Hyj.*, 1943, **34**, 327) points out that on oxidation the pH falls to 4–5 and then dispersion occurs.

Soil Reaction and Plant Disease.

In yet another sphere soil reaction may influence the yield of our agricultural crops, *viz.*, in its effect on the incidence or severity of many plant diseases.   At the moment there is very little detailed information on this point, but it is a safe prediction that a more general understanding of this question will become a powerful weapon in the hands of those who seek to control the fungus and bacterial diseases of plants.   Probably the best-known instance of the interrelationship of soil reaction and plant disease is that of " Finger and Toe," which is so prevalent in kale, cabbage, swedes, and other plants of the order *Brassicæ*, when grown on acid soils. This disease is extremely rare in neutral or alkaline soils, but is very persistent on acid soils.   Even the common practice of avoiding disease by including susceptible crops in rotations only at long intervals fails in this case.   So far as is known the only safe remedy lies in correcting the soil reaction.   As a result of the extreme sensitivity of this disease to soil reaction its appearance has long been regarded as an infallible indication of sourness. Again both wart and scab diseases of potatoes are well known to be far more prevalent in neutral and alkaline soils than in acid ones, and this, coupled with the fact that the optimum growth range for potatoes is below pH 6·0, is strong evidence in support of the long-established practice in cropping of " keeping lime and potatoes as far apart as possible " in the rotation.   As examples of more recent investigations on the correlation of plant disease and soil reaction may be mentioned the work of Sherwood on the *Fusarium* wilt of tomatoes.   This disease is most prevalent in acid soils, but by the addition of increasing amounts of lime the percentage of attacked plants was steadily reduced to a minimum, which corresponded with a soil reaction of pH 7·4.   Again, the " black root rot " of tobacco has been shown to cause severe injury to plants growing in soil of pH greater than 5·9, whereas on soils with pH less than 5·6 the disease is rare, and even when observed

does little damage (Doran, *J. Agric. Res.*, 1929, **39**, 853). Instances of preliminary investigations of this kind might be multiplied at great length but the whole question is little understood, and cause and effect are in many cases not easy to distinguish. Doubtless in many cases the disease organisms are directly influenced by changes in soil reaction, but it must also be borne in mind that variations of reaction even when not far removed from neutrality may profoundly alter the conditions of plant nutrition ; and this, in turn, does much to weaken the plants' natural resistance to infection. This phase of the general question of soil reaction is one which invites deeper investigation with every assurance of fruitful results.

Theories of Soil Acidity.

From the above it is seen that the reaction of a soil is intimately connected with plant growth in a number of ways, and that any marked deviation from the neutral point brings with it the probability of decreased crop yields which become more and more affected as the pH value of the soil diverges from the range 6·5 to 7·0. Extremes of soil reaction on the alkaline side are relatively less widespread, and, moreover, the causes, rectification, and effects on plant growth bring the investigator into spheres of physico-chemical inquiry in which hydrogen-ion concentration plays little part. The so-called " alkali " soils will not, therefore, be considered here. The consideration of acid soils, and the measurement of acidity, for the purpose of arriving at satisfactory ameliorative measures, has demanded much more detailed investigation, and in this matter the measurement of hydrogen-ion concentrations has figured largely. The experimental aspect of soil acidity, itself a complex problem, is rendered more difficult by the impossibility in many cases of the isolated study of a particular series of changes, in which there is little or no measured control of interdependent reactions and effects. As a result existing theories of soil acidity are largely the outcome of repeated attempts to correlate experimental data which in many cases have no common basis. The International Society of Soil Science has done much to bring together the widely scattered soil scientists of the world and to derive from discussion clearer ideas on many soil problems. The reports of the Society on the meetings at Groningen in 1926, when the whole problem of soil acidity was given much consideration, are an important milestone in the progress of this branch of agricultural chemistry. It can hardly be stated that we have arrived at a clear-cut understanding of the detailed chemistry of soil acidity, but we have, to say the least.

gone far towards reaching generally accepted ideas which can form the foundation of practicable methods of measuring and explaining the nature of soil reaction.

It is both interesting and instructive to recall some of the theories put forward from time to time in explanation of the phenomena of " sourness " in soils. The presence of free mineral acid in soil has long been discredited even when coupled with the selective absorption theory. The occurrence of organic acids can, however, be definitely proved and offers a somewhat more practicable basis of consideration. In highly organic soils acidity may be partially or wholly the result of the presence of such bodies.

The degree of acidity of organic soils, is, generally speaking, much smaller than in many mineral soils where only small amounts of organic matter exist. Moreover, recent work shows very definitely the close relationship between the clay fraction of mineral soils and the phenomena of base exchange, adsorption and soil acidity. Treatment of acid soils with neutral salts results in many cases in the disappearance (adsorption) of some part of the added basic ions and the development of further acidity in the solution. The latter is attributed by many workers to the hydrolytic acidity of aluminium salts which appear in the solution. This may be ascribed to the result of a base exchange action, or to the solvent action of the soil complex of the acid, liberated through the adsorption of basic ions from the neutral salt.

The known toxicity of aluminium salts and the fact that this can be corrected by treatment with lime and with phosphates in water cultures as in the soil (Mirasol, *Soil Sci.*, 1920, **10**, 153 ; Hartwell and Pember, *Soil Sci.*, 1918, **6**, 259) led to the fairly widespread acceptance of the theory that the toxic factor in acid soils was aluminium. Closer investigation of the soil conditions from the point of view of hydrogen-ion concentrations reveals certain points which make it difficult to reconcile this theory with actual facts. The work of Britton on the electrometric titration of aluminium salt solutions with lime and with silicates (see Chapters X and XXV) indicates that equilibria included in the quaternary system $CaO—Al_2O_3—SiO_2—H_2O$ are most likely to control the solubility of aluminium salts in soil. The precipitation of aluminium hydroxide by lime begins at pH 4·2 and by silicate at 4·0 to 4·1. Moreover, in the lime titrations the redissolution of aluminium as calcium aluminate does not commence in solutions with lower pH values than 8 to 10. It is to be concluded, therefore, that in soils of pH values 4·0 to 8·0 little or no aluminium can be present in the dissolved state. Magistad

brings forward data (*Soil Sci.*, 1925, **20**, 181) showing the improbability of the existence of more than 3 p.p.m. of soluble aluminium in soils of *p*H values 4·7–8·0. These contentions are largely supported by the analyses of displaced soil solutions by Pollard and his co-workers at the Imperial College of Science, London. No appreciable amounts of aluminium were found in soil solutions above *p*H 4·0 ; and on limed soils *p*H values of 7·5 to 8·0 were reached before aluminium again appeared in the soil solutions. On recently limed soils of *circa* *p*H 9·0 approximately 30 p.p.m. of aluminium were detected in the soil solution. These facts, coupled with a number of American investigations in plant culture and field work, tend to throw doubt on the belief in the toxicity of aluminium in acid soils.

From time to time suggestions have been advanced as to the existence in soils of active alumino-silicic acids which by reason of their nature might well be concerned in controlling soil reaction. They have also been regarded as amphoteric bodies existing in a state of combination which results from a form of dynamic equilibrium with dissolved ions in the soil (Loew, *Porto Rico Expt. Sta. Bull.* 13, 1913). More recently, the tendency to identify alumino-silicic acids with the active substance in soil clay has been more pronounced. There is a tendency nowadays to regard the work of Bradfield (*Missouri Agr. Exp. Sta. Research Bull.*, No. 60, 1923 ; *J. Amer. Chem. Soc.*, 1923, **45**, 2669) as consolidating this view. He concluded from a comparison of the properties of soil colloids, separated from clay, with those of a mixture of hydrated silica, alumina, and ferric oxide, that the colloidal material consisted either of a definite compound or of a mixture of compounds in which the oxides were chemically bound as alumino-silicates. The type of titration curve obtained with the hydrogen electrode when a solution of calcium hydroxide was titrated with a clay suspension was considered to be that of a weak acid, and he was therefore led to believe that the colloidal material in the soil was itself the acid. Saint (*Trans. 2nd Comm. Internat. Soc. Soil Sci.*, Gröningen, 1926, 134) has suggested that if a soil be represented as a partly neutralised acid, the amounts of different bases which any particular soil can absorb should be in equivalent proportions, and has advanced evidence to support the view in the case of the alkalis and the alkaline earths when considered separately, the difference between the two sets of figures being attributed to the formation of insoluble alkaline-earth salts. This, however, would be expected from a consideration of the very similar reactions which the alkaline earths and the alkalis enter into with hydrated silica.

The reaction involving the formation of the aluminium silicate precipitate affords no evidence of the existence of a complex alumino-silicic acid (Fig. 173). It is true that if the changes in hydrogen-ion concentration are followed when such a precipitate is subjected to treatment with 'solutions of alkalis or alkaline earths, the precipitate exerts a pronounced buffer action, which *prima facie* might be regarded as indicating that the precipitate was an acid. This buffer action is, however, the result of the superposition of several reactions, *viz.*, (*a*) the reaction between the aluminium hydroxide and the base to form a soluble aluminate, buffering between pH 8 and 10 ; (*b*) the reaction between the base and the hydrated silica, giving rise to a gradual rise in pH from 6 upwards ; and (*c*) an equilibrium between the silicic acid and any soluble aluminate, *e.g.*, $Ca(AlO_2)_2$, which may have been initially formed, to give calcium silicate, $CaO,xSiO_2,yH_2O$, and hydrated alumina, producing a hydrogen-ion concentration from pH 6 upwards. The amount of soluble aluminate actually formed is doubtless a function of the amount of water present. Similarly, if the inorganic colloids of the soil be considered mainly as mixtures of hydrated alumina and silica, then the effect on the hydrogen-ion concentration of adding slaked lime to the soil would be determined by the reactivity of the two constituents with the lime. The titration curves of soil suspensions as obtained by Hissink and van der Spek (*Trans. 2nd Comm. Internat. Soc. Soil Sci.*, Gröningen, 1926, 72) with the hydrogen electrode all show buffer action between pH 6 and 8.

Whichever view may be accepted it is clear that any question of the physical adsorption of basic ions by clay may, to a great extent, be discarded, and the reactions between soil and dissolved salts may be regarded as chemical processes.

The conceptions, however, of Gedroiz in Russia and by Hissink in Holland as to the nature of soil acidity and the related phenomena of base exchange and " adsorption " are built somewhat on the assumption of the presence of alumino-silicic acid in the soil. Briefly, the clay particle is regarded as consisting of an alumino-silicic acid substance presenting an outer layer of colloidal gel as its active surface and in which most of its chemical reactions are localised. Hissink regards this outer layer as the seat of an electrical double layer on the internal side of which are concentrated negative alumino-silicate ions, and on the outer side the positive ions of the soil bases (Ca, Mg, Na, K) and of hydrogen. These latter ions are concerned in base-exchange phenomena. The relative proportions of the individual ions are dependent on local soil conditions and are represented as being in equilibrium

with the ions dissolved in the soil water which surrounds the clay
particle. Soil conditions conducive to a high concentration of a
particular ion in the soil solution bring resulting interchanges
among the ions of the electrical double layer and an increase in
the proportion of the particular ion therein. Thus the addition
of (say) potassium chloride to a soil results in an increase in the
proportion of potassium ions in the clay system and the appearance
of an equivalent proportion of calcium and other ions in the soil
solution. Moreover, by repeated leaching of a soil with potassium
chloride solutions it is possible step by step to replace practically
the whole of the basic ions of the clay by potassium ions and to
obtain what is described as a " potassium soil." This process is
of course reversible, and we must assume the existence of " calcium
soils," " sodium soils," etc., characterised largely by differences
in physical properties. It is not to be supposed that the relative
proportions of basic ions in solution and those in the clay complex
are directly proportional. On the contrary, the ease of displace-
ment of one ion by another varies considerably. Thus a definite
ionic concentration of $K^{\cdot}$ in the soil water produces a much
greater displacement of calcium ions from the clay than would
a similar ionic concentration of $Na^{\cdot}$. The ease of displacement
of the common ions would appear to be in the order,

$$Ca^{\cdot\cdot} > Na^{\cdot} > NH_4^{\cdot} > K^{\cdot} > H^{\cdot}.$$

On the basis of the complex alumino-silicic acid hypothesis, it
is to be assumed that acidity of the clay particle as a whole will
depend on the relative proportions of base and hydrogen ions, and
that those in turn are in equilibrium with base and hydrogen ions
dissolved in the soil water. That this equilibrium is not a simple
one is shown by the fact that the same relative change in pH
value of the soil extract does not produce proportionally similar
changes in the base : hydrogen ratio as determined by Hissink
(see later). These observations harmonise better with the view
that the soil colloids are simply mixtures of hydrated alumina and
silica. Below pH 7 there is a distinct tendency for the aluminium
hydroxide to retain varying quantities of acids as basic salts, which
on treatment with bases will undergo decomposition. Above the
neutral point, bases react with both components forming both
insoluble and soluble silicates and possibly aluminate.

The curves given in Fig. 173 also account for the presence of
various metals in soil solutions of different pH values. As already
stated aluminium is only found in a soil solution whose pH value
is either less than about pH 4 or greater than pH 8. Many
chemists have also found alumina in the neutral-salt extracts of

sour soils ; thus, by the use of potassium chloride or nitrate, sodium chloride, etc., Veitch (*J. Amer. Chem. Soc.*, 1904, **26**, 637) concluded that the addition of sodium chloride to a soil did not liberate hydrochloric acid as such but aluminium chloride, and therefore the acidity was only apparent. Knight's (*Ind. Eng. Chem.*, 1920, **12**, 343) analysis of a soil extract with potassium nitrate shows that 90 per cent. of the titratable acid was in combination with alumina. Rice (*J. Physical Chem.*, 1916, **20**, 214) found aluminium in potassium nitrate extracts of which the pH's ranged from 3·5 to 4·5. . Niklas and Hock (*Z. angew. Chem.*, 1925, **38**, 195) titrated potassium chloride extracts of soils with sodium hydroxide, using the hydrogen electrode. The first branch of their curve, corresponding to the decomposition of the aluminium salt, lies at about pH4 (compare Fig. 123), and the remaining section shows a buffer action up to just above pH 8. The acidity of the more acidic soils is due to the normal hydrolysis of the aluminium salts formed in the soil.

The pH of soil solutions from sour soils after treatment with neutral salts often becomes still lower ; thus Crowther (*J. Agric. Sci.*, 1925, **15**, 212) found that soils of pH 4·78 on treatment with neutral salts gave about pH 4. Soils of pH $>$ 6 appear to be unaffected by neutral salts, and their titratable or " mineral " acidity becomes negligible (compare Christensen and Jensen, *Trans. 2nd Comm. Internat. Soc. Soil. Sci.*, Gröningen, 1926, 111). The mineral acidity given by acid soils appears to depend on the extent to which neutral salts, when allowed to react upon soils, are able to cause an increase in hydrogen-ion concentration above that requisite for the precipitation of aluminium hydroxide, and thereby to enable alumina to pass into solution as a salt. The fact that the hydrogen-ion concentrations of such soil solutions are nearly the same as that at which aluminium hydroxide is normally precipitated suggests that the soil must contain some aluminium hydroxide in a partly neutralised state (*vide* p. 70). This would, on hydrolysis through contact with water, give a pH near that at which aluminium hydroxide becomes precipitable. When a neutral-salt solution is added to such a soil, it is probable that the salt splits up, the basic part combining with the preponderance of silicic acid and being retained by the soil, and the acidic part combining with the partly neutralised aluminium hydroxide to enable some aluminium salt to pass into solution. Thus sodium chloride might be considered to split up into sodium oxide and hydrochloric acid, the sodium oxide attaching itself to the large excess of colloidal silica and thus becoming insoluble, whereas the hydrochloric acid, in reacting with the aluminium hydroxide,

causes some aluminium chloride to pass into solution and thereby increases the hydrogen-ion concentration and the titratable acidity. It is significant that this " exchange " acidity disappears almost completely from soils of pH 6 and above. It is at this point that aluminium hydroxide acquires its optimum insolubility, due to the withdrawal of the small amount of acid radical which it retained on being precipitated. Above this point, it behaves as an acid and consequently is without effect on neutral salts.

A system of characterising the acid condition of mineral soils in terms of the following factors has been suggested by Goy, Müller and Roos (*Z. Pflanz. Düng.*, 1929, **13A**, 66) : (1) *Total acidity*, determined by electrometric titration to pH 7·7. This comprises the " exchangeable acidity," found by titrating a soil suspension in a solution of potassium chloride, and the " hydrolytic acidity." (2) The existing pH of the aqueous soil suspension. (3) The pH of the soil in potassium chloride solution. (4) Buffer value for the total acidity, expressed as mg. NaOH required to neutralise 1 mg. of hydrogen ion. (5) Buffer value for the exchange acidity, *i.e.*, to pH 5·0. (6) Buffer value for the hydrolytic, or residual, acidity, pH 5·0–7·7.

Manganese has been found in solutions from certain acid soils. Pollard (private communication) has found it in solutions of pH up to 6 from certain sour soils. Sufficient manganese to be toxic to plants was observed by Wallace *et al.* (*A. Rpt. Agric. Hort. Res. Station*, Bristol, 1946, 61) to be present in reclaimed heathland, of which the pH was 4. Rice (*loc. cit.*) found it in potassium nitrate extracts up to pH 5 of acid soils. Fig. 136 shows that the precipitation of manganese silicate does not begin until just above pH 7. The pH of manganous salt solution is of the order 5 to 6, but it must be remembered that, when a manganous salt solution is treated with alkali in a quantity insufficient to start precipitation, the solution rapidly decomposes through oxidation and brown oxide separates. Hence it is unlikely that manganese would be found in a soil solution of pH $>$ 6.

Although ferric oxide is often a constituent of soils, very little can pass into the soil solution, except in colloidal form, because it is precipitated from strongly acid solutions (Britton, *J. Chem. Soc.*, 1925, **127**, 2155). In soils containing humus it is extremely probable that the humus brings about the reduction of the ferric hydroxide to ferrous hydroxide which, as will be understood from Table 165, will more readily dissolve. It can, however, sometimes be detected in the neutral-salt extracts of sour soils by testing with an alcoholic solution of potassium thiocyanate (Comber's test).

Pollard (private communication) found that by adding hydro-
chloric acid to soils, the iron content of the aqueous extracts only
became perceptible when the solutions had become more acid
than pH 1·5.

The phenomenon of base-exchange in soils has been attributed
by Raman to the existence of zeolitic combinations in the inorganic
colloidal matter, in spite of the fact that zeolites themselves do
not occur in soils. As will be evident from page 139, the active
constituents of soils and zeolites are the same, to which in all
probability the " base-exchange " exhibited by both must be
attributed. Trénel and Wunschik (Z. Pflanz. Düng., 1930, **17A**,
257, 296) state that probably no alumino-silicic acid exists,
for when the bases have been partially removed permutite behaves
as a mixed gel of hydrated alumina and silica. Exchange acidity
represents the varying degrees to which the reaction :

$$KCl + Al(OH)_3 \rightarrow AlCl_3 + 3KOH \qquad \text{proceeds.}$$
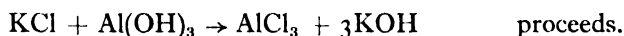
The question of the nature of the operative factor in acid soils,
which brings about plant injury, is still not definitely answered.
The presence of neither free mineral acid nor of aluminium salts
can be satisfactorily substantiated experimentally. Are we to
suppose the hydrogen ion itself is a plant poison or indeed are the
ill-effects on plant growth of acid soils really the effects of a poison
in the true sense of that word ? To distinguish direct toxicity
from injury through some secondary effect is a difficult matter.
It has been suggested that, in the absence of definitely poisonous
materials in acid soils, it may well be that conditions conducive to
an excessive proportion of hydrogen ions in the soil may also
affect the proportions of other cations in a manner which militates
against satisfactory plant nutrition. Obviously the plant growing
in soil does not absorb and utilise the minerals in the soil solution
in whatever proportions they occur. The present conception of
the nutritive process, as being akin to ionic transmission through
the semipermeable membranes of the root tissues, must include
a recognition either of the mutual effect of the various ions on the
rate of their diffusion, or of some internal mechanism of the plant
giving some measure of control of the nature and proportion of
the ions entering the root hairs. It is then conceivable that the
presence of excessive proportions of hydrogen ions or, alterna-
tively, of conditions producing them, may influence the diffusion
of one or more of the mineral nutrients to an amount which
induces malnutrition of the plant. It is known, for example,
that the phosphorus intake of plants is fairly sensitive to changes
in pH of the nutrient medium, and also that the rate of absorption

of certain cations by the root hairs increases with decreasing pH values of the nutrient.

Availability of Nitrogen—Nitrogenous Fertilisers

Under anaerobic conditions nitrogenous fertilisers have different effects on the soil reaction. Thus ammonium sulphate, Leuna saltpetre, " Ammophos," Nitrophoska and urea tend to impart lower pH values to the soil; nitrates of sodium (Chile saltpetre) and calcium and calcium cyanamide tend to raise the pH, and blood meal and cotton-seed meal are without appreciable effect. The effect of ammonium sulphate to lower the pH of soils is illustrated in Table 225, which is based on observations of Pierre (*Ind. Eng. Chem.*, 1931, **23**, 1440). The figures in the last column give some idea of the buffering exerted by the soil.

TABLE 225

pH OF SOILS AND INFLUENCE OF AMMONIUM SULPHATE

| Soil. | pH | | | Lb. $(NH_4)_2SO_4$ per Acre to bring to pH 4·8. |
	Untreated Soil.	500 lb. per Acre $(NH_4)_2SO_4$.	1000 lb per Acre $(NH_4)_2SO_4$.	
Norfolk Sand	5·85	5·00	4·80	1000
Ruston Sandy Loam . .	5·40	4·65	4·35	342
Cecil Clay Loam . . .	6·15	5·88	5·60	4290
Mississippi Delta Soil .	6·00	5 63	5·23	2000

Hence the need for the application of lime with the ammonium sulphate. In their initial actions, urea and cyanamide are both " physiologically alkaline," but ultimately they become " physiologically acid " and the net result in the case of urea is to lower the pH value of the soil, whilst in the case of cyanamide the pH is only slightly raised, owing to the lime initially liberated by hydrolysis by the acid subsequently formed. Nehring (*Landw. Jahrb*, 1929, **69**, 105; *Bied. Zentr.*, 1929, **58**, 390) observed that these characteristics were greatest in humus, sandy loam pot cultures, at pH 4–5 with sodium nitrate; at pH 6 with urea and calcium cyanamide together; at pH 7 with urea alone; and at pH 8 with ammonium sulphate. He claims that below pH 6·5 nitrate-nitrogen is a better plant food than ammoniacal nitrogen; but that above pH 6·5 the two forms are of equal value. Similar observations have been made by Fresenius (*Z. Pflanz. Düng.*, 1930, **17A**, 176) on the crop yields of oats and barley on different

soils that had been limed to varying extents. Larger yields were given by sodium nitrate and these are reflected in the higher pH values set up. In some light soils, however, which had received ammonium sulphate the fertilising effect was able to overwhelm the effect of the 'lower pH.

The production of an acid reaction in soil by the so-called physiologically acid fertilisers has been traced to the acid developed from them by nitrification. The nitrogen assimilated by the plant is absorbed in the nitrified form. Hence the efficiency of such fertilisers is connected with the extent to which nitrifying processes can take place in the soil, and these have been found to be largely dependent on the pH value and consequently on the degree of saturation of the soil with lime. For this reason not all the nitrogen put into the soil in the form of ammonium sulphate is usually absorbed. When applied as sodium nitrate the nitrogen is in a form that is probably assimilated as such, leaving the soda in the soil to increase the pH. The original pH value of the soil can be maintained by adding either ammonium sulphate and a suitable amount of calcium carbonate or ammonium sulphate and sodium nitrate. Pierre (J. $Amer$. Soc. $Agron$., 1928, 30, 254, 270) found that the acid-producing tendency of part of the ammonium sulphate could be counteracted by 1·2 parts of calcium carbonate, instead of the 1·5 parts required to form calcium sulphate and calcium bicarbonate. This is due to incomplete nitrification of the ammonia. A mixture of 3 parts of sodium nitrate to 1 part of ammonium sulphate maintained the original reaction of cropped pots.

The loss of nitrogen from soil, either as such or in the form of gaseous compounds, is largely a matter of acidity or alkalinity. Thus Tovborg-Jensen and Kjaer (Z. Pfl. $Ernähr$. $Düng$., 1950, 50, 25) found that when sulphate of ammonia was added to calcareous soils the losses of ammonia became significant when the pH was higher than 7. When it was added to sandy soils considerable loss, as nitrogen, occurred if the pH lay between 4·5 and 5·5, but this was not so when the pH was 6·5–6·8. A probable cause is the formation of ammonium nitrite and its subsequent decomposition (Gerretsen, $Versl$. $Landbouwk$. $Onderzoek$., 1949, 54, 16; $Trans$. $4th$ Int. $Cong$. $Soil$ Sci., 1950, 2, 114). Jones ($Soil$ Sci., 1951, 71, 193), by using tracer technique, has shown that nitrogen lost, under anaerobic conditions, from a soil at pH 4–6 originated almost entirely from nitrate, probably through bacterial denitrification. Another possible cause of loss of nitrogen is the reaction between nitrite and amino groups. Thus Allison and Doetsch ($Proc$. $Soil$ Sci. Soc., $Amer$., 1950, 15, 163)

found that at pH 4·5 nitrite does react with alanine but not above pH 5·2. Such an interaction is hardly likely to take place in soils to any extent.

Some experiments, carried out by Prianischnikow (*Biochem. Zeitsch*, 1929, **207**, 341) on the grôwth of sugar beet and maize in sand cultures, in which the soil reactions were kept approximately constant, show that at pH 7·0 ammonium sulphate yielded better results than did sodium nitrate, but at pH 5·0 the ammonium sulphate was much less satisfactory than sodium nitrate. Coupled with the poorer results given by ammonium sulphate at pH 5, it was also found that the plants contained much less calcium. The addition of lime to the soil at pH 7 increased the fertilising power of the sodium nitrate, but had no effect on that of ammonium sulphate. It must be mentioned, however, that even if the soil is maintained at pH 7 and at the same time is deficient in calcium ions the fertilising action of ammonium sulphate will be very much reduced. Unsuitable hydrogen-ion concentration, or a deficiency of nutrient inorganic matter may restrict the synthesis of carbohydrate by the plant. In these circumstances it becomes susceptible to " ammonium-poisoning," and this may occur whatever form of nitrogenous fertiliser may have been applied.

Nitrates not only promote the excellent growth of meadow grass (*Poa pratensis*) but they exert a maximum effect over the soil pH range of 4·5–6·5, whereas ammonium salts show a very narrow optimum range in the immediate vicinity of pH 6·5 (Darrow, *Bot. Gaz.*, 1939, **101**, 109.)

Availability of Phosphorus.

The hydrogen-ion concentrations of soil solutions play an important rôle in rendering any phosphorus the soil may contain available to the plant. Britton (*J. Chem. Soc.*, 1927, 620) has calculated from the data of Bassett (*ibid.*, 1917, **111**, 624 ; *Z. anorg. Chem.*, 1908, **59**, 1) relating to the ternary system, $CaO—P_2O_5—H_2O$, that calcium phosphate, either the di- or tri-phosphate, is not precipitated from solutions which are more acid than pH 5·5 (approx.). Addition of slaked lime converts the $CaHPO_4$, first precipitated into $Ca_3(PO_4)_2$ without any apparent change in pH, and this in turn may be rendered basic to an extent corresponding to $3Ca_3(PO_4)_2,Ca(OH)_2$, called " hydroxyapatite " by Bassett, with a change in pH to 5·9. (See Chapters X and XXVII.)

The foregoing is of interest on account of its bearing on the reactions which take place in soils when treated with phosphatic

fertilisers. If the pH of the " soil solution " falls below 5·5, the calcium phosphate in the soil will pass into the soluble state, though when in this condition there will be a great tendency for some of the phosphate to suffer " reversion " through reaction with colloidal alumina, but when lime is added so as to raise the pH to 5·5 and above, the phosphate begins to become insoluble, initially as the dicalcium salt, and finally as the basic phosphate. It is probable, as stated by Bassett, that " hydroxyapatite " is the phosphate which exists permanently in soils under ordinary conditions, for any di- or tri-calcium phosphate, which may first be formed, will ultimately become decomposed.

Soil solutions in equilibrium with the dicalcium phosphate contain relatively large amounts of partly neutralised phosphoric acid which, when removed, either by " reversion," or by the plant, or by drainage, will cause the solid phases to decompose and eventually to become basic without any great change in pH taking place. The conversion of the phosphate into the insoluble basic state renders it unavailable to the plant. Thus Gedroiz (*Zhur. Opit. Agron.*, 1911, **12**, 529) found that tri-calcium phosphate gave the best immediate results on soils not saturated with bases. The necessity of having the soil just on the acidic side of neutrality has been emphasised by von Wrangell (*Landw. Vers.-Stat.*, 1920, **96**, 1), who recommends the use of " physiologically acid fertilisers," such as ammonium sulphate, to render any phosphate available.

The ease with which aluminium phosphate becomes decomposed on decreasing the hydrogen-ion concentration, even though the reagent used may itself be a soluble phosphate, throws some light on the manner in which vegetation obtains its phosphorus from the soil. The electrometric curve in Fig. 138 shows that aluminium phosphate undergoes appreciable decomposition on adding sodium phosphate, so much so that on the attainment of about pH 9 the precipitate began to redissolve. Miller (*Soil Sci.*, 1928, **26**, 435) has studied the decomposition of aluminium phosphate by alkali. Between pH 3·0–4·5 no decomposition occurred, but about pH 4·5 gradual decomposition took place and some phosphate passed into solution as the alkali salt. At pH 7·5 the alumina also began to dissolve, and at pH 8·5 the dissolution of the basic aluminium phosphate became complete. When a soluble phosphatic fertiliser, such as superphosphate of lime, is added to a soil, and especially if the soil be sour, " reversion " of the phosphate occurs through the formation of insoluble phosphate on the surfaces of the colloidal particles of hydrated alumina and ferric oxide (see, *e.g.*, Lichtenwalner, Flenner and Gordon, *Soil Sci.*, 1923, **15**, 157 ; Hall and Vogel,

ibid., p. 367). Marais (*ibid.*, 1922, **13**, 355), in a study of the application of aluminium phosphate as a fertiliser, concluded that, in spite of its low solubility in citric acid, it is of service in soils well stocked with lime, but should never be used on acid soils unless lime is applied in intimate contact with it. Slaked lime causes aluminium phosphate to decompose with the formation of soluble calcium phosphate until pH 5·5 is reached. Phosphate fixation is stated to be the least severe at pH 6·5 by Williams (*N.A.A.S., Quart. Rev.*, 1949, **1**, 147).

Soils, rich in ferric oxide and alumina in the hydrated and reactive form, convert phosphatic fertilisers into phosphates of aluminium and ferric iron. It is these phosphates that determine the phosphate solubility in ordinary soils. According to Gaarder (*Medd. Vestlandets Forstl. Forsøksstat.*, 1930, No. 14), soils rich in these " active " sesquioxides render the phosphate largely insoluble over the entire range pH 4·0–7·5, and liming does not always effect an improvement. In semi-humid and humid soils, however, the humus present in combining with some of the phosphate renders it soluble. Should these soils have only moderate sesquioxide contents and be of pH 4·5–6·5 there is a risk of the organically combined phosphorus being leached away, thereby causing a phosphate deficiency. Bobko and Maslova (*Trans. Sci. Inst. Fertilisers*, Moscow, 1926, No. 39) studied the ease with which phosphate could be extracted from various types of soil by means of N/10 hydrochloric acid. A forest loam (pH 6·8) gave up phosphate with very little acid, whilst chernozem and podsolised loam at pH 5·9 to 6·8 did not give up any phosphate until pH 4·0 was reached, and a sandy soil did so only at pH 2·5. Regarding the absorption of phosphate by maize and wheat plants from culture solutions, Tidmore (*Soil Sci.*, 1930, **30**, 13) observed that greater absorption took place from acid nutrient solutions than from alkaline solutions, but the variation in pH from 4 to 6 had very little effect on the rate of absorption. A method, due to Neubauer, of estimating the amount of available phosphorus and potassium in soils is based on the amounts taken up by rye seedlings during a short period of growth in a mixture of the soil, undergoing test, and sand. Using this method with arid soils Sekera (*Z. Pflanz. Düng.*, 1928, **7B**, 525) found that acid conditions facilitated phosphate absorption. In alkaline soils the solubility of phosphates falls below the minimum required for plant growth. Acid soils showed potash deficiency.

In regard to the availability of phosphorus some attention must be directed to the part that may be played by organic phosphorus compounds that may be present in the soil, for

Jackman and Black (*Soil Sci.*, 1952, 73, 117, 167, 179) state that the phosphorus, which such compounds contain, does not become available to plants until they have been converted into inorganic phosphates. They found that the phytase activity, which is possessed by soil bacteria and fungi, occurs within the range, pH 5–7, it being greatest at pH 5 and least at pH 7. The probable reason for this is that fungi flourish more at pH 5, which produce more phytase than do bacteria. The action of phytase, however, is restricted somewhat owing to the relative insolubility of phytates and the salts of the lower inositolphosphoric acids. Thus in the presence of an excess of their respective metal-ions, ferrous phytate is insoluble between pH 2·5 and pH 8·0 ; aluminium phytate within the range, pH 3·0–9·0 ; calcium phytate at pH > 6·0 and magnesium phytate at pH > 9·7. Both the salts of the lower inositolphosphoric acids and the corresponding phosphates are more soluble than the respective phytates. Inasmuch as the solubility of the various salts and the consequent phytase activity render the phosphorus available to vegetation, it follows that it is desirable to maintain the soil at pH 6.

Some phosphatic fertilisers have an effect on the soil reaction and at the same time on the amount of available calcium. Thomas and Elliot (*J. Soc. Chem. Ind.*, 1929, **48**, 51T) state that superphosphate is without effect in a poor clay loam, dissolved bones only effect a slight increase in available calcium, and basic slag gives a slightly increased pH and a large increase in calcium. The calcium was estimated by Hissink's method, p. 427. In the tea soils of N.E. India, Harler found that (*J. Ind. Tea Assoc.*, 1928, 199) basic slag and Belgian phosphate caused significant increases in pH values and decreases in exchange acidity as determined by Hopkins' method of extraction with potassium nitrate solution. Superphosphate, bone-meal and Algerian phosphate gave only slight increases in pH.

Good tea soils should have a pH value of about 6, and their potassium nitrate extracts should lie between pH 4 and 4·8. The soils of Assam used for the production of tea and indigo are rich in available phosphate. According to W. R. G. Atkins, Assam soil has a pH of 5·4, which thus explains the availability of phosphate. The acidity was due to the oxidation of sulphur originating from the iron pyrites contained in the soil. The development of acidity in soil may be induced by treatment with sulphur, which may undergo not only direct oxidation but oxidation promoted by sulphur bacteria. It is not surprising therefore to find that soluble phosphate manures have been prepared by composting sulphur and phosphatic manure.

The assimilability of potash and phosphates by roots in arable soils of various types has been found by Gracanin and Němec (*Z. Pflanz. Düng.*, 1930, **9B**, 126) to be increased within the range pH 4·4–6·9 by adding lime. Soils from pH 7·4–8·3, already containing 5–13 per cent. CaO, underwent a reduction in their root-soluble phosphate content. The availability of phosphorus in fertilisers is usually considered to be indicated by their solubility in acids, *e.g.*, citric. Dirks and Scheffer (*Land. Jahrb.*, 1930, **71**, 74), however, call attention to the fact that the root-sap of plants has a higher pH value than the solvents commonly employed, and advocate the use of a calcium bicarbonate solution saturated with carbon dioxide as being more satisfactory.

Determination of the Lime Requirement of Soils.

The development of ideas on the cause and effect of sourness in soils is reflected in the methods which have from time to time been adopted for its measurement. This has resolved itself into the more practical process of measuring the amount of lime necessary to counteract this fault—the lime requirement. Earlier methods were simple and direct but empirical. In a general practical way soils, which contained no carbonates as shown by the absence of effervescence with acid, were deemed to need lime. More accurate measurements of a quantitative nature involved the determination of the amount of lime which the soil could absorb (*e.g.*, Veitch, *J. Amer. Chem. Soc.*, 1902, **24**, 1120) or of the quantity of carbonate or bicarbonate of calcium, with which the soil reacted, as measured by the evolution of carbon dioxide (Hutchinson and MacLennan, *J. Agric. Sci.*, 1915, **2**, 25; MacIntyre, *J. Assoc. Off. Agric. Chem.*, 1915, 417; and Knight, *Ind. Eng. Chem.*, 1920, **12**, 340, 457, and 559). These methods have been of very considerable value, more particularly in recent years when the cost of transport and distribution of lime has assumed greater relative importance. From a scientific standpoint such methods leave much to be desired. The equilibrium between soil—CaO—CO_2—$CaCO_3$ has been shown to be sensitive to changes of external conditions (Crowther, *J. Agric. Sci.*, 1925, 201 *et seq.*), and it is evident that the wide discrepancies between the various methods (Fisher, *J. Agric. Sci.*, 1921, **11**, 19) are in part due to this fact and partly to the different processes not all leading to the measurement of the same basal reaction. As a result, a comparison of the lime requirement of different soils by the same process and of the same soil by different processes is impossible. The best value can only be obtained in this way, if used in conjunction with soil survey maps by workers of experience.

The base-exchange theory of soil acidity is illustrated by lime-requirement methods of Hopkins (*U.S. Dept. Agri. Bur. Chem. Bull.*, 73 (1903)); Jones (*J. Assoc. Off. Agric. Chem.*, 1915, **1**, 43), and Daikuhara (*Bull. Imp. Cent. Agric. Exp. Sta. Japan*, 1914, **2**, 1), in all of which the acidity developed by treating soil with solutions of salts is measured, and later by Comber who measures acidity by the ferric thiocyanate coloration produced by the liberation of iron from acid soils by neutral salt treatment.

A number of indirect methods for measuring the hydrogen-ion concentration of soils has been advanced, *e.g.*, those involving the inversion of cane sugar, the hydrolysis of esters and the decomposition of iodide-iodate solutions (Baumann and Gully, *Exp. Sta. Record*, 1908, **19**, 1008).

Later came the refinement of the technique in the direct determination of pH values, and the many attempts to correlate pH and lime requirement. The definite association of " sourness " and " acidity " had persisted throughout years of investigation, and much enlightenment was expected from research, in which actual hydrogen-ion concentrations could be accurately measured. Practical measurements of pH values in soils are made either by the colorimetric methods of Clark and Lubs (*J. Bact.*, 1917, **2**, 1, 109, 191), or the simplified method of Gillespie (*Soil Sci.*, 1918, **6**, 219), or preferably, where accuracy is more important, by direct electrometric methods, using a hydrogen, glass or quinhydrone electrode. The last named process is that devised and adapted for soil measurements by Biilmann (*J. Agric. Sci.*, 1924, **14**, 232 ; see also Biilmann and Jensen, *Trans. 2nd Comm. Internat. Soc. Soil Sci.*, B., 1927, 236). It is more rapidly performed than with types of apparatus utilising hydrogen electrodes, and except for its limitation on the alkaline side of pH 8·0 is as satisfactory. Probably the best hydrogen-electrode apparatus for the purpose is that devised by Crowther (*J. Agric. Sci.*, 1925, 15) and illustrated here.

The special features of the apparatus are :—

(1) The electrode vessel (D) and the platinum electrode are both large and continuously rocked so as to secure rapid equilibrium between the hydrogen and the soil suspension.

(2) The junction between the soil suspensions and the saturated potassium chloride connecting solution is made below a three-way tap in a bent syphon tube. In this way the entrance of potassium chloride into the electrode vessel is prevented and a wide well-mixed liquid junction is obtained. Any soil flocculated below the three-way tap is caught in special traps (E).

(3) The reservoir (B) provides for the use of both a saturated
   calomel electrode and a standard N/10 calomel electrode
   (A), the latter being provided with the Koehler device
   for preventing diffusion from the saturated potassium
   chloride solution.

(4) Two determinations may be made simultaneously.

(This particular apparatus as supplied by Messrs. Gallenkamp
contains a Clark's rocking hydrogen electrode shown as F;
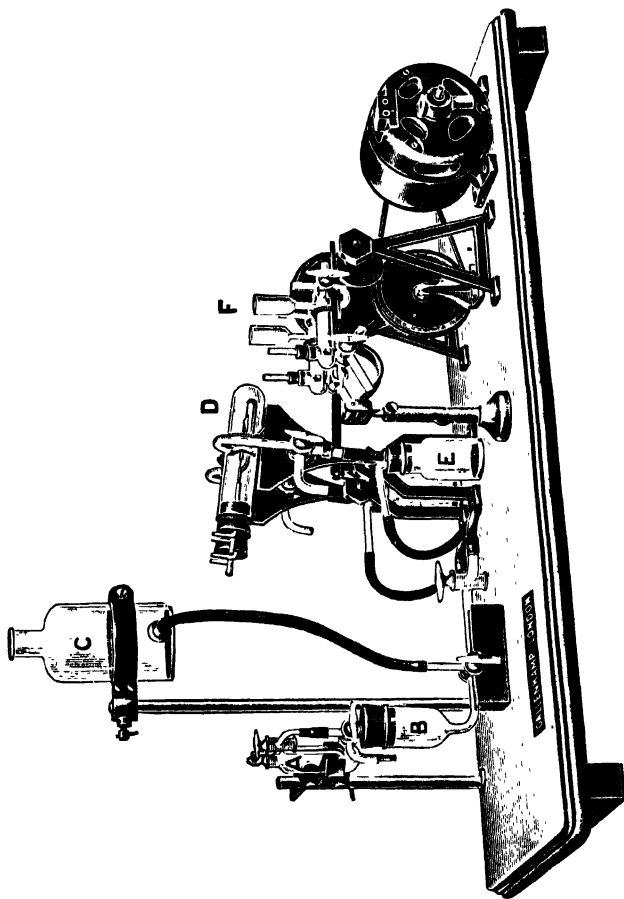
FIG. 187.—Crowther's Apparatus.

see Fig. 187.) Whilst the apparatus adopted for hydrogen-ion
measurements is now of a high order of excellence, details of

technique have hardly reached a satisfactory standard. A considerable amount of discussion has arisen from time to time as to the manner in which the soil sample should be prepared for pH determinations.

No satisfactory means are available for measurements in the soil *in situ*—obviously the ideal method—and we are limited to the examination of soil extracts, on the manner of preparation of which much depends. If water extracts are made, the question of the proportion of soil to water used is important. Crowther has recommended a ratio of 1 : 5 for the purpose, but in very many cases a smaller ratio of 1 : 2·5 or 2·0 is adopted in the belief that a fairer representation of the true value is thus obtained. On the assumption that there exists in soil an equilibrium between the dissolved cations and those intimately associated with the clay particles but not in true solution, there is to be considered the possibility of a disturbance of this equilibrium following the addition of water to the soil, so that the pH value of the extract may differ from that of the natural soil. The extent of the displacement of the equilibrium depends largely on the nature of the soil itself and the ratio of soil : water used. A moderate ratio (up to 1 : 5) does not markedly affect the observed values of most soils of pH values 6 to 7, but tends to give low values on the acid side and high values on the alkaline side of this range. Wide ratios of soil : water usually tend to yield observed values nearer to the neutral point than those found when small proportions of water are used. The proportion of carbon dioxide in soil influences the results obtained in wide ratio extracts to a marked extent. Thomas and Elliot (*J. Soc. Chem. Ind.*, 1931, **50**, 303T) prefer to use small ratios of soil : water, such as 1 : 0·5, 1 : 1 and 1 : 1·5. The soil is stirred with the water for 30 seconds, quinhydrone added and the pH measured in 5–20 minutes. (See also Salter and Morgan, *J. Physical Chem.*, 1923, **27**, 117 ; Snyder, *J. Agric. Res.*, 1927, **35**, 825 ; Terlikovski, *2nd Comm. Internat. Soc. Soil Sci.*, 1927, B, 151.)

Bray (*Ind. Eng. Chem.*, 1928, **20**, 421) has devised a simple form of hydrogen electrode vessel, shown in Fig. 188, in which he measures the hydrogen-ion concentration of soil suspensions that are kept in a state of constant agitation by the passage of hydrogen. To carry out a measurement 10 grams of soil are mixed with 25 c.c. of distilled water, and after the gas has been passed for 13 minutes the salt-bridge is connected and a reading taken, and then another 2 minutes later. He emphasises the fact that the pH of the supernatant liquid will be somewhat different from that obtained before the soil particles are allowed to settle.

A difficulty encountered, however, is that the moving particles tend to wear the electrodes bright.

Again there arises the question as to whether the soil extract should be filtered, or centrifuged or whether the actual soil suspension should be used. Filtering has been discredited owing to observed alterations in the pH value of the extract during passage
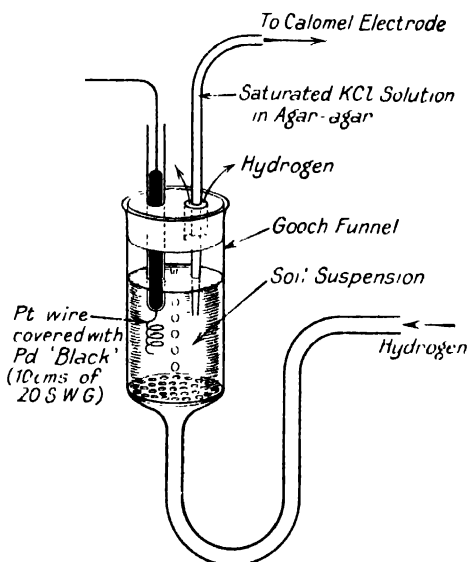
FIG. 188.—Bray's Form of Hydrogen Electrode Vessel.

through the filter paper, and similar though smaller changes are recorded, when the suspension is centrifuged. In some cases these differences are large, *e.g.*, the values for a number of soils examined by means of suspensions were in the range pH 4·1 to 5·0, but when the suspensions were filtered or centrifuged the range of observed values rose to 6·2 to 7·4. These discrepancies are largely reduced by thoroughly shaking the soil suspension. It is suggested by way of explanation that the colloidal coatings of the soil particles of the surface exposed on a filter paper or centrifuge tube to the aqueous extract, may act as a semipermeable membrane and allow unequal diffusion between the soil mass and the extract, thus causing alterations in the hydrogen-ion concentration of the latter. Shaking, by disrupting this membrane, leads to the maintenance of a more steady value in the extract. It has been observed that similar changes in pH

values occur in dilute salt solutions exposed to gelatinous aluminium and ferric hydroxides.

Determination of pH values of soils, especially those containing manganese dioxide, by means of quinhydrone, may often be too high. Errors as high as 1·8 pH have been recorded. (See for example Heintze and Crowther, *Trans. 2nd Comm. Internat. Soc. Soil Sci.*, Budapest, 1929, A, 102 ; Karraker, *J. Amer. Soc. Agron.*, 1930, **22**, 171). S. Kühn (*Z. Pflanz. Düng.*, 1929, **15A**, 13) considered it to be much less exact and reliable than the indicator method. With certain soils quinhydrone led to indefinite and irregular pH values. He states that carefully crystallised quinhydrone imparts a definite acid reaction to a soil suspension, it alone setting up a pH of 3·4 approx. Soil suspensions used in pH measurements should be well stirred, for on settling the supernatant liquid often has a lower pH than the soil (*cf.* Smolik, *Internat. Soc. Soil Sci.*, 1930, **5**, 9 ; Wiegner and Pallmann, *ibid.*, 1929, B, 92).

Some investigators prefer to substitute a neutral salt extract for a pure water extract in pH determinations specifically designed for the calculation of lime requirements as bringing into effect the exchange acidity of Kappen (*Z. Pflanz. Düng.*, 1924, **3A**, 209). From this point of view the method may have certain advantages, but it would seem preferable to adopt the simple water extract as giving results approaching more closely the actual pH value of the natural soil.

For the practical purpose of determining lime requirements some connexion has been sought between the existing soil reaction and the amount of lime required to bring this to neutrality. Both theory and observation pronounce this impossible. All soils have considerable but widely differing buffer capacities, *i.e.*, they contain active material tending to counteract changes in reaction brought about by the addition of basic or acid substances. Apart from the small amounts of dissolved buffering salts (phosphates, carbonates, salts of organic acids, etc.) and possible reserves of calcium carbonate, both the clay and the humus act as buffering agents with considerable effect. The known variation in the proportions of the latter in various soils is sufficient to preclude any possible relationship between the existing pH value of an acid soil and its lime requirement. The *modus operandi* of any determination of lime requirement based on hydrogen-ion measurements must be in the nature of an electrometric titration to a definite pH value.

No standardised practice has as yet been adopted. Apart from variations in observed pH values brought about by modifications

in technique above referred to, there are additional debatable points as to correct procedure. A strict comparison between laboratory and field liming operations introduces obvious difficulties in the matter of the distribution of lime in the soil in the laboratory and the control of its reaction with soil in the field under similar conditions. To titrate a soil suspension with lime introduces the possible error due to the use of soil : water ratios which are never obtained in the field, and in addition the reaction end-point would probably not be the same in both cases. Similar but uncontrollable errors may intervene if extracts of soil treated with dry lime, as in the field, are examined. In the latter case, too, the time of reaction is prolonged to varying extents in different soils and some kind of arbitrary standard is demanded. Satisfactory measurements can be made, by a standardised laboratory technique yielding data, from which the amount of lime required in the field can be calculated. Christensen and Jensen have
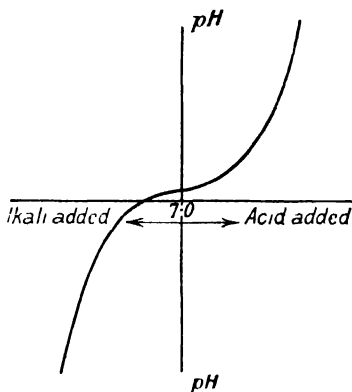
Fig. 189.—Buffer Curve of Soil.

elaborated a method (*Trans. 2nd Comm. Internat. Soc. Soil Sci.,* 1926, A, 94) whereby the soil is titrated with lime water to a *p*H value of 7. The amount of lime so needed multiplied by 3 (the " liming factor ") gives a reasonably close approximation of the true lime requirement. The " liming factor "—obtained by purely empirical means—is doubtless accounted for by the less even distribution of lime in the field and its less rapid reaction with the soil, combined with losses of lime by drainage to subsoil, etc., during the reaction period. Before leaving the matter of electrometric soil titrations, reference should be made to another valuable measurement—the " buffer capacity " of soil. This value is represented by Jensen (*Intern. Mitt. Bodenk,* 1924, **14,** 112) in the form of a graphical surface area. The *p*H values of a number of soil samples treated with increasing amounts of acid and alkali are determined. The curves interpreting the results are of the form shown in Fig. 189.

The area lying between this titration curve and the base curve of a buffer-free soil is the buffer capacity. The buffer capacity represents the ability of the soil to withstand changes of reaction

and gives expression in a concrete form to the possibility of a soil becoming acid in the near future, or, alternatively, some conception of the period for which a given lime treatment is likely to suffice.

Brief reference should be made here to the methods of Hissink and Gedroiz for determining lime requirements, although actual measurements of hydrogen-ion concentrations are not involved. The method is based on a consideration of the clay (or humus) particle and its surrounding double ionic layer described previously. The clay particle carrying a definite charge is associated with a definite equivalent of cations in the outer shell. The total base equivalent, with which the clay can combine, is designated " T," the amount of a particular base ion present as " S." The condition of the clay particle is represented as the degree of saturation

" V " where $V = 100\dfrac{S}{T}$. This is to be considered as the per-

centage of the maximum possible basic ions which are actually present under the conditions of experiment. Smaller values of V correspond with smaller amounts of basic ions present and therefore with larger proportions of hydrogen ions in the clay complex and hence greater acidity. Experimentally the calcium values are measured. The value " S " is obtained by prolonged leaching with ammonium chloride, and a determination of the calcium so removed. T - S is obtained by titration with free base to complete saturation, *i.e.*, to the pH desired in the soil. From these figures the value " V " is calculated. It is calculated that V for neutral soil is approximately 55 per cent. Hissink has shown general relationships to exist between the values V, S, and the pH value and calculates his lime requirement as that required to produce pH 7·0. The general application, however, of these values to all soils leads to some conflict of opinion (*cf.* Sigmund, *Proc. 2nd Comm. Internat. Soc. Soil Sci.*, 1926, A, 55).

A rapid measurement of lime requirement can be made, according to Hardy and Lewis (*J. Agric. Sci.*, 1929, **19**, 17), by shaking 10 grams of soil with 40 c.c. of neutral 0·2 M.-calcium chloride solution and then titrating with 0·03 N-lime-water in successive portions of 5 c.c., with three minutes shaking after each addition until pH 7 is passed. The amount of lime required can be calculated from the volume of lime-water used in bringing the mixture to pH 7. The pH measurements are made with the quinhydrone electrode.

From the foregoing it is clear that, in the general problems of plant nutrition and of microbiological activities in the soil

and within the plant tissue, the reaction of soil and plant sap is of vital importance. Data obtained have already enabled great advances to be made in this sphere and continued investigation must inevitably enhance our knowledge of the vital processes. In the study of soil chemistry in general, and of the problem of sourness in particular, much has been gained from the investigations of the causes and effects of changes in hydrogen-ion concentration, the importance of which as a factor in the chemical evaluation of soil fertility is now generally recognised.

pH and Soil Analysis.

A method, due to Olsen (*Comp. rend. Trav. Lab. Carlsberg*, 1929, **17**, No. 15), for the estimation of ammonia in soil consists of shaking with N-potassium chloride after adding sufficient hydrochloric acid to bring the pH of the soil suspension to about 1, and distilling off the ammonia from the filtrate to which magnesia has been added.

Calcium in soils and plants in the presence of iron, aluminium, titanium, manganese, magnesium and phosphates may be completely precipitated as oxalate from a boiling solution whose pH value has been adjusted to 4 by means of ammonium chloride (Chapman, *Soil Sci.* 1928, **16**, 479).

For the micro-estimation of sulphate, see page 204.

HYDROGEN-ION CONCENTRATION AND CERAMICS

EXCEPT for small amounts of oxides of iron, titanium, calcium, and the alkali metals, clay comprises mainly hydrated alumina and silica. Though its composition is not by any means constant, those varieties which are used in the ceramic industry correspond to formulæ ranging in silica-content from

$$Al_2O_3,1\cdot5SiO_2,2H_2O \text{ to } Al_2O_3,3SiO_2,2H_2O.$$
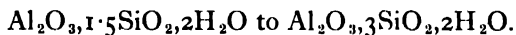
The ideal clay is usually considered to have the composition shown by the formula of kaolin, $Al_2O_3,2SiO_2,2H_2O$. Clay is probably more than a simple mixture of two colloidal hydrated oxides, for there is good reason to believe that chemical forces, though certainly very weak, exist between some of the weakly basic alumina and some of the weakly acidic silica. Thus we saw on page 132 that the precipitate obtained by adding a dilute " water-glass " solution to one of aluminium sulphate is a basic aluminium silicate, which begins to separate from solution at pII 4. It is surprising that the precipitate should have been basic, in view of the fact that the sodium silicate solution used contained a large proportion of silica. Schwarz and Brenner (*Ber.*, 1923, **56**, B., 1433) also found that the precipitates obtained with sodium silicate from aluminium chloride solutions contained silica in amounts slightly greater than required by $Al_2O_3,1\cdot5SiO_2$. Using a great excess of reagent the dried precipitate approximated to $Al_2O_3,2SiO_2,2H_2O$. This precipitate, however, differed from kaolin in that it was decomposed by concentrated hydrochloric acid with comparative ease. Though the samples were shown by means of X-ray spectrographs to be amorphous after ageing for periods up to 8 days, it was observed that thereafter they began to assume a crystalline structure similar to that of kaolin. In ordinary clay the effects of ageing become very marked, as may be seen from their enhanced resistance to attack by concentrated solutions of acids and alkalis. Nevertheless, clay may be acted upon by acids and alkalis, though with dilute solutions the reactions which occur can hardly be described as other than incipient. Small as they are, the addition of reactants in small concentrations to clay suspensions, which vary the hydrogen-ion

concentration, results in appreciable physical changes in the colloidal solutions.

Clay is composed of fine-grained particles whose surfaces have become more easily attackable through the action of water and weather. These fine particles are thus covered with a film of colloidal aluminium hydroxide and silicic acid, and it is the reactions into which they can enter with the various flocculating and deflocculating agents that determine the properties of " clay-slips " and of clay. The various stages of the reactions involving these substances are controlled by the hydrogen-ion concentration
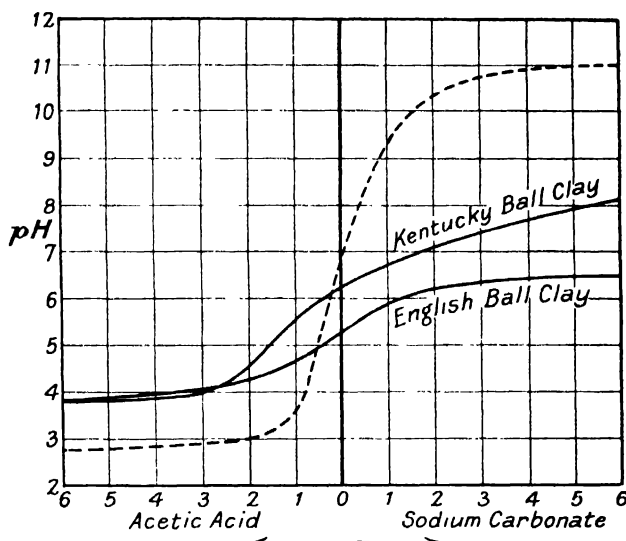
FIG. 190.—*p*H of Water-Clay Extracts on Treatment with (1) Acetic Acid (2) Sodium Carbonate.

which the reagents are capable of setting up. It is therefore probable that *p*H measurements will assume greater importance in pottery work, though it must be conceded that the results of the few workers who have interested themselves in this problem sometimes appear to be conflicting.

An idea of the nature of the reactions of clay with acids and alkalis may be obtained from Fig. 190, in which are shown the variations in *p*H of water-clay extracts, 12 : 1, caused by the addition of acetic acid and sodium carbonate. The broken line shows the effect of adding these reagents to water alone. The curves were taken from a paper by Randolph and Donnenwirth

(*Jour. Amer. Cer. Soc.*, 1926, 9, 544). The acid branches of the curves refer to the interaction of the aluminium hydroxide gel with the acetic acid, and it is interesting to note that throughout the major part of the reaction the *p*H was about 4. Such a value would be expected, for the aluminium salt formed must have been in equilibrium with an excess of undissolved aluminium hydroxide, and thus the conditions were not very different from those ruling for the reverse reaction, *viz.*, that of precipitation. Considerable action occurred between the clay and the sodium carbonate, as shown by the position of the titration curves compared with the broken-line curve. The buffered curves show that equilibria must have been set up between the silica and the hydrolysed sodium hydroxide, though the low *p*H values indicated were probably the result of the action of some acid, which the clay originally contained in combination with the alumina gel. The fact that clay on treatment with water gives rise to extracts whose *p*H values generally lie between 4 and 5 (Hall, *J. Amer. Cer. Soc.*, 1923, 6, 991) suggests that the dissolved portions must be soluble basic aluminium salts (compare p. 70), and as the solutions thereby obtained are colloidal, it appears that some kind of equilibrium must exist between the colloidal particles and the solutes. We might therefore regard particles of clay as being made of more or less insoluble nuclei of differing grain size surrounded by a colloidal film containing silica, alumina, some basic aluminium salt and water. On coming into contact with water some of this basic aluminium salt passes into solution, establishes an ionic equilibrium between the liquid and solid phases, in which micellar ions of clay particles play a considerable part, tending to stabilise the colloidal solution. Clays of alkaline reaction probably contain no basic salt but instead contain some silica in combination with alkali or alkaline earth in a soluble condition. According to Hall's data aqueous clay extracts may have *p*H values ranging from 3 to 8·4. The hypothesis here advanced accounts for Hall's observation that in general a clay, which gives an acid extract with the first addition of water, will decrease in acidity as successive amounts of water are added, and that clays giving an alkaline extract usually decrease in alkalinity on washing.

Plastic clay is, of course, clay in the flocculated condition. The degree of plasticity of a clay is the factor on which many of the desired properties of the finished article seem to depend. Plasticity refers to the effect of pressure applied to clay and the deformation which is thereby effected. It may be that the cohesive forces, which exist between the clay particles, are involved in the question of the amount by which clay can suffer alteration in

shape without falling apart. The forces of cohesion and capillarity operate when the particles are sufficiently close to one another, and it is in this regard that the size and nature of the colloidal film, and also the size of the insoluble clay particles become of importance. Hydrogen-ion concentration may prove to be an effective factor in the control of these surface films. Various methods have been adopted to secure control of the plasticity of clays, based on the power of the colloidal matter to adsorb various salts and dyes and also on the viscosity of the clay-slips. If water is added to clay it becomes increasingly plastic, until an amount is added which results in stickiness. Thereafter, more water produces a clay suspension, known as the clay-slip.

Where articles are manufactured by casting, the production of efficient clay-slips becomes a matter of vital importance. Thus according to Mellor ("A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. VI., 489), a clay-slip prepared with about 0·3 per cent. of a mixture of sodium carbonate and silicate can be readily poured in casting operations, though it may contain less water than a stiff mass of clay which has not been treated with alkaline solution. On adding a little acid to the clay-slip in an amount sufficient to neutralise the alkali it contains immediate "solidification" ensues, so that the vessel can be inverted without spilling the contents. If more alkali be now added the clay assumes its former fluid condition, though the amount of alkali mixture to be added varies from clay to clay. Randolph and Donnenwirth (*loc. cit.*) state that the addition of small amounts of acid or alkali affects the viscosity of the clay-slip and the way in which it acts in the casting mould, so influencing the plasticity and strength of the dry clay. Electrolytes present in the clay often have an effect on the strength of the clay pieces in the dry state. The viscosity—*p*H relationship differs from clay to clay, but nevertheless it may prove to be of considerable use in connexion with the particular batches of clay for which they may be determined. Due to the complex physical nature of clay it is likely that *p*H data will have to be considered in conjunction with other properties, *e.g.*, rate of settling, soluble matter, contraction and strengths in the dried and fired conditions when fired at different temperatures. Fessler and Kraner (*J. Amer. Cer. Soc.*, 1927, **10**, 505) could, however, find no relationship between *p*H data and viscosity or other properties. Randolph and Donnenwirth concluded that there was a relationship between the *p*H of the slip and the breaking strength of the finished clay-ware ; they found that the maximum strength occurred in those

products prepared from slips at pH 6, irrespective of the acids used.

The rate of settling of a clay suspension is a function of the pH of the medium, in that it affects viscosity by promoting the dissolution of colloidal matter at certain pH ranges. At pH values below 4 aluminium hydroxide passes into true solution and at values higher than about pH 9 slow dissolution of the silica occurs, though it does not become considerable until an alkalinity of the order of pH 12 has been acquired. Hall (*J. Amer. Cer. Soc.*, 1923, **6**, 991) found that the maximum rate of settling lies between pH 2·7 and 4·0 (see also Olof Arrhenius, *J. Amer. Chem. Soc.*, 1922, **44**, 521). As this range lies immediately below the aluminium hydroxide precipitation pH, it appears that the settling out of the particles must be due to the partial removal of the colloidal layers from the surfaces of the clay particles in forming a less viscous solution. He found that the range for maximum deflocculation (*i.e.*, peptisation) was pH 10 to 12, which was caused by a steady reaction of the alkalis with the clay. This action may be accounted for by the formation of clay micellar anions, through the initial adsorption of the alkali and the subsequent partial dissolution and ionisation of some of the sodium clay complex.

The pH of clay-slips which are to be used for casting lies between 5·5 and 9·3. For the manufacture of goods not necessitating the use of pure clays the most suitable pH will usually be found to lie in the lower half of this range. This applies to fire clays. For purer clays, *e.g.*, white clays, the optimum pH is higher, and lies somewhere above the neutral point.

As recommended by W. A. Taylor (" The A B C of Hydrogen Ion Control," La Motte, 1928, p. 46), the water in which a clay body is suspended can usually be separated by filtration through an alundum filtering cup under air pressure applied above and around the cup. The clear solution thus obtained may be used for the colorimetric determination of pH.

* * * * *

The production of finely divided calcium carbonate is of importance in the manufacture of plate glass. A suitable product may be obtained by precipitation from a solution of calcium chloride by means of sodium carbonate and sufficient alkali to impart to the mother-liquor a pH between 9·5 and 11·5. The grinding of the precipitate should be carried out with water adjusted to the same pH (B.P. 479,054).

CHAPTER XLVI

HYDROGEN-ION CONCENTRATION AND THE TEXTILE AND DYE INDUSTRIES

THOUGH the value of the control of hydrogen-ion concentration in textile processes is only just beginning to be realised, the investigations which have hitherto been carried out indicate that it is a matter of definite practical importance. This applies more particularly to the wet processing of the ampholytic substances, silk and wool, and especially to their dyeing.

Among other substances, acids and alkalis may have a particularly deleterious effect on the proteins of wool and silk by promoting their hydrolysis. Such damage, which is often difficult to detect, may render the fibres susceptible to attack by the chemicals in the later processes, and thereby impair the finished product as regards its tensile strength, elasticity, and wearing qualities. Though examination of the fibres under the microscope will reveal damage when it has advanced sufficiently far, it cannot be relied upon for the detection of an incipient attack. Thus the damage of wool fibres caused by acid begins on the epithelial scales, which through their resulting wrinkling, are visible through the microscope as striations, whilst continued hydrolysis causes them to disintegrate, and finally to dissolve. The damage done by alkalis is more difficult to observe since their attack is initially localised on the cortex, which may even be dissolved out without any appreciable effect on the epithelial scales.

Wool is an ampholyte. According to Elöd (*Z. angew. Chem.*, 1925, **38**, 837, 1112; *Z. physikal. Chem.*, 1928, **137**, A, 142) its isoelectric point is at pH 4·9 at 20° and at pH 4·6 at 90°. Speakman (*J. Soc. Dyers and Colourists*, 1925, **41**, 172) found that at pH 4·8–4·9 no combination occurs between the ferrocyanide ion and wool. Wool undergoes minimum swelling at pH 4·8 (Speakman and Stott, *Trans. Faraday Soc.*, 1934, **30**, 539) and Dumanski and Dumanski (*Koll.-Z.*, 1934, **66**, 24) found that fine wool fibres do not migrate in an electric field at pH 4·9. On the other hand, Meunier and Rey (*Compt. rend.*, 1927, **184**, 285) observed minimum swelling at pH 3·6–3·8; Harris (*Bur. Stand. J. Research*, 1932, **8**, 779) found that wool particles suspended in various buffer solutions exhibited no electro-migration

at pH 3·4, and Skinkle (*Amer. Dyestuffs Repr.*, 1934, **25**, 1) showed that it has maximum yarn strength at pH 3·2–3·6.

The fact is that, if there is an isoelectric point, it is not well-defined, and as Speakman and Stott (*Trans. Faraday Soc.*, 1935, **31**, 1435) have demonstrated, by the electrometric titration of wool with different acids and bases, wool, in common with other animal fibres (Lloyd and Bidder, *ibid.*, 864), possesses an iso-electric range from pH 5 to pH 7, within which almost no combination with acids and bases actually occurs.

An ingenious explanation why such an isoelectric range should exist has been advanced by Speakman and Hirst (*ibid.*, 1933, **29**, 162). They assume that the peptide chains in wool are linked across by salts of histidine, arginine and lysine on the one hand, with aspartic and glutamic acids on the other. Six types of salt linkages are thus possible, each salt possessing its own isoelectric point. Using the following values for the dissociation constants :—histidine, $K_b = 5·7 \times 10^{-9}$; arginine, $K_b = 1·0 \times 10^{-5}$; lysine, $3·2 \times 10^{-5}$ and glutamic acid, $K_{a_1} = 6·3 \times 10^{-5}$; aspartic acid, $K_{a_1} = 1·5 \quad 10^{-4}$, the isoelectric points can be calculated

from
$$[H^+]_{I\text{H}0} = \sqrt{\frac{K_a}{K_b} . K_w}$$

Isoelectric Point.

thus :
Histidine-aspartic acid	.	.	.	pH 4·79
histidine-glutamic acid	.	.	.	pH 4·98
Arginine-aspartic acid.	.	.	.	pH 6·41
arginine-glutamic acid	.	.	.	pH 6·60
Lysine-aspartic acid .	.	.	.	pH 6·66
lysine-glutamic acid .	.	.	.	pH 6·85

Speakman and Townend (*Trans. Faraday Soc.*, 1936, **32**, 897) have shown than an isoelectric range also exists with feather keratin from pH 4 to pH 8.

It is therefore desirable to have a means by which the amounts of acid and alkali in wool fibres can be detected and estimated. King (*J. Soc. Dyers and Colourists*, 1927, 321) has devised a method based upon the buffering effects which these impurities may have on the hydrogen-ion concentration of acetic acid, and the shade of colour assumed by the fibres when dyed with certain of the sulphone-phthalein indicator dyestuffs. The dyeing is performed at room-temperature with a suitable indicator in a bath containing acetic acid equal in weight to 1 per cent. of the weight of the wool, after which the temperature is very slowly raised to the boiling-point.

Table 226 gives some idea of the percentage amounts of acid which can be estimated from the tints of the dyed wool.

TABLE 226

PERCENTAGE OF ACID IN WOOL

Indicator.	Colour Change with Increasing Concentration of Acid.	Percentage of Sulphuric Acid (on Dry Weight of Wool).
Thymol blue	Yellow-orange red-magenta red	4·5–7
Bromophenol blue . .	Blue-greenish blue-yellow . .	3–5
Lacmoid	Slate blue-puce red	1·5–3
Bromocresol purple . .	Purplish-dirty blue-yellow . .	0–2
Bromothymol blue . .	Bluish-green-yellow	0–1

Wool, silk and Nylon begin to absorb caustic soda at pH 7 and after a slow increase the absorption rapidly rises at pH 11·5 to saturation at pH 13–13·5.   Strong acids, however, are absorbed below pH 0·8 and the absorption reaches a maximum at pH 1·3 (Elöd and Frölich, *MelliandTextilber.*, 1949, **30**, 103, 249, 405, 579 ; Elöd and Zahn, *ibid.*, 349).

In American specifications for cloth a pH requirement is usually included.   Such an estimation may be made by means of suitable indicators, *e.g.*, bromothymol blue, phenol red, cresol red and thymol blue.   An electrometric method in which the glass electrode is used has been described by Wakeham and Skau (*Ind. Eng. Chem., Anal. Edn.*, 1943, **15**, 616) for the determination of the pH of cloth.   It is cut up into small pieces and soaked in a small volume of distilled water, previously boiled and cooled. After 20 minutes about 1 c.c. of water is squeezed out of the cloth and its pH measured.   The water is then returned to the cloth and more water is also added (1 c.c.).   After 15 minutes another 1 c.c. of water is pressed out and its pH determined.   This process is repeated many times, adding increasing volumes of water each time.   The observed pH values are plotted against the total volume of water present at any given time, 3, 4, 5, 7, 10, 15, 20, 30, 50 and 100 c.c. and extrapolation to zero volume gives the pH of the cloth.

The reaction between bisulphites and wool involves the disulphide linkings and in so doing impairs the strength of the fibres, the maximum weakening occurring at pH 4·5 and pH 11. (Stores, *Trans. Faraday Soc.*, 1942, **38**, 261).   Middlebrook and Phillips (*Biochem. J.*, 1942, **36**, 428), however, found that

only one half of the cystine sulphur in wool reacts with sodium bisulphite at pH 5.

Treatment of wool fibres with formaldehyde (*ibid.*, p. 294) not only strengthens them but decreases their susceptibility to attack by chemicals, although this resistance depends on pH and temperature. Thus at pH 5·6 the temperature must be raised to 70° C. before the bisulphite reacts and then about one third of the total disulphide sulphur becomes involved.

The rôle of basic groups in the combination of protein fibres with dyes is clearly demonstrated by Fraenkel-Conrat and Cooper (*J. Biol. Chem.*, 1944, **154**, 239), who found that the amounts of dyes of opposite charges absorbed by various proteins corresponded with the total number of acidic and basic groups present. Thus the total number of polar groups in egg albumin, as determined analytically, is the same as that calculated from the amounts of Orange G absorbed at pH 2·2 and of Safranine O absorbed at pH 11·5.

Combination of formaldehyde with proteins reduces the acidic and basic dye absorption, but the N-methylene and N-methylol groups thereby produced retain sufficient basic strength to combine at pH 2·2 with Orange G.

The problem of the reaction of formaldehyde with wool has been attacked more directly by Steinhardt, Fergitt and Harris (*J. Biol. Chem.*, 1946, **165**, 285) who estimated the amounts of hydrochloric acid and potassium hydroxide which combine with wool within the range, pH 3·0–13·3, in the absence, and in the presence, of formaldehyde, 0·25–1M. The differences point to the combination of the formaldehyde with the amino-groups of lysine and there are indications that the guanidino-group of arginine may be involved.

According to Alexander, Carter and Hudson (*J. Soc. Dyers Col.*, 1949, Apr.) wool can be rendered non-felting by treatment with dilute solutions of permanganate below pH 2. Although the reaction is one of oxidation of the disulphide linkage only slight damage is done to the wool.

In general, acid dye-baths may have as high an hydrogen-ion concentration as pH 1·5 without incurring any serious harm. This, however, should be regarded as a limiting value. The extent of alkalinity varies with the different types of fabric. For example, cotton will stand solutions of pH up to 12 or 13 without any great risk ; in fact, alkaline solutions of such a pH value, on account of their rapid action, are used for the removal of impurities. Regarding the finishing of wool and silk, it is found that both too little and too great an alkalinity of the respective

scouring and degummirfg baths lead to unsatisfactory results. For wool scouring, a soap solution containing sufficient soda to raise the pH to between 10 and 11 is used, though the temperature should not be allowed to go beyond 60° C.   In the degumming of silk pH 10 is required.   The distortion of fabrics caused during scouring may be rectified by winding on a roller and boiling in water maintained at pH 6 (Whewell and Bee, *J. Soc. Dyers Col.*, 1946, **62**, 178).

As scouring agents, synthetic detergents as a class are excellent in removing oil and grease, but their suspending power for dirt is inferior to that of soap.   In this respect, however, their performance can be improved by adjusting the solution to approximately pH 11 by the addition of sodium carbonate (*vide* Hill and Hunter, *Nature*, 1946, **158**, 585 ; Desseigne, *Mem. Serv. Chim.*, 1944, **31**, 347).

In the degumming process of silk, sericin, oil and natural pigments are removed.   Mosher (*Proc. Amer. Assoc. Textile Chem. Colorists*, 1930, 193 ; *Amer. Silk J.*, 1930, **49**) finds the sericin can be completely removed from silk by boiling in solutions of pH greater than 9·5 or less than 2·5.   At pH values higher than 10·5 and lower than 1·7 the silk rapidly loses in strength. He gives pH 10-10·5 as the optimum for scouring silk.   Regarding silk-degumming by means of proteolytic enzymes, Meunier and Vallette (*Russa*, 1930, **4**, 1513) found that Codex pancreatin acquires its maximum degumming activity on Italian yellow gum silk at about pH 8.   Pancreatin has practically no effect on fibroin whatever may be the pH.   The swelling of fibroin at pH 8 is less than that of ordinary silk.   Two strains of aerobic bacteria have been isolated from the liquors used in the fermentative degumming of waste silk by Katagiri and Nakahama (*J. Agric. Chem. Soc.*, Japan, 1937, **13**, 1003 ; 1938, **14**, 243).   They are similar to *B. cereus*, the active agent being the enzyme, " degummase," which attacks both sericin-A and sericin-B but not fibroin. Its maximum activity is at 40° at pH 7-8.   Two forms of sericin, A and B, are believed to exist, the A form being soluble in hot water, whilst the B form is but sparingly soluble.   It is, moreover, more resistant to proteolytic enzymes (Kaneko, *ibid.*, 1933, **9**, 905).   Mosher (*Canad. Text. J.*, 1934, **51**, 31) claims to have identified yet another, sericin-C, which is insoluble in all common solvents and is not attacked by enzymes.

The swelling of degummed mulberry silk fibres has been investigated by W. S. Denham and Dickinson (*Trans. Faraday Soc.*, 1933, **29**, 331 ; *Bull. Sericult.*, Japan, 1932, **4**, 1), who observed minimum swellings at pH 1·4, 2·8, 3·8 and 4·7, the

swelling being least at pH 3·8. From cataphoresis and flocculation experiments on fibroin suspensions, Hawley and Johnson (*Ind. Eng. Chem.*, 1930, **22**, 297) concluded that an isoelectric range existed from pH 1·4 to pH 2·8. Other values given for the isoelectric point are : Chinese mulberry silk fibroin, pH 2·4-2·6, Tussah fibroin, pH 4·2-4·4 (Wang and Woo, *J. Chinese Chem. Soc.*, 1937, **5**, 170), pH 2·85 (Shozo and Bito, *Bull. Sericult.*, Japan, 1931, **4**, 2) ; fibroin, pH 4·6 (Rastelli, *Koll.-Z.*, 1934, **67**, 55), pH 5·1 (Dumanski and Dumanski, *ibid.*, 1933, **66**, 24), pH 4·2 (Meunier and Ray, *Compt. rend.*, 1927, **184**, 285) ; pH 3·8 (Denham and Brash, *J. Text. Inst.*, 1927, **18**, T 520.)

The dependence on pH of the oxidising action of the hypochlorite ion is discussed in Chapter XXXVIII. It is necessary to consider not only the oxidation of the colouring matter, but the possible oxidation of the fibre itself. The maximum rate of oxidation of cellulose occurs at pH 7 and as Nabar, Scholefield and Turner (*J. Soc. Dyers and Colourists*, 1937, **53**, 5) state, that in order to minimise any deterioration of cotton threads, the hypochlorite bleach should not be allowed to fall below pH 9. Wasser (*Textilber.*, 1936, **17**, 219, 326) found that sodium hypochlorite is a more effective bleaching agent at pH 9·6 than at pH 6·9. On the contrary, Elöd and Vogel (*ibid.*, 1937, **18**, 64) obtained greatest whiteness at pH 7-8 and least at pH 5 and at pH 10. These observations, however, refer to rapid bleachings, when the bleaching occurs superficially on the threads. They do not take into account of the degradation of the cellulose threads, which must occur. Slower acting bleaching liquors, *i.e.*, at higher pH values, give in longer time a more complete bleach, unaccompanied by an excessive degradation. Buffering with magnesia at pH 9 has been suggested by Davidson (*J. Text. Inst.*, 1933, **24**, T 185).

The application of pH control to peroxide bleaching liquors has been investigated by Trotman and Trotman (*J. Soc. Dyers and Colourists*, 1926, **42**, 154). They found that the best bleaching, together with the least amount of structural change in the fibres, is obtained at pH about 10. (See also Elöd and Vogel, *loc. cit.*) Incidentally this pH is economical when the amount of bleaching agent is taken into consideration. This explains why sodium perborate is an efficient bleaching agent, as in solution it undergoes hydrolysis and so maintains a pH of about 10. The prolonged action of oxidising agents on the cystine in wool is illustrated by the work of Smith and Harris (*Bur. Stand. J. Res.*, 1936, **16**, 301) who found that wool treated with two-volume hydrogen peroxide at 50° for three hours undergoes little change

between pH 1 and 7, but suffers rapid attack above pH 7, as shown by a decrease in the cystine content (Campbell, *Amer. Dyestuff Repr.*, 1936, **25**, 67P).   Claron (*Russa*, 1930, **4**, 1531), inserts other buffer agents such as soap, silicate and carbonate, apparently to stabilise the pH of the liquors.   The adjustment of the pH of peroxide baths may have an important effect on retarding their decomposition.   Thus Ra (*Z. ges. Textil-Ind.*, 1929, **32**, 262) found that sodium peroxide solutions containing sulphuric acid and sodium pyrophosphate and buffered with ammonia to pH 7·6 underwent less than 1 per cent. decomposition at 60° C. after five-and-a-half hours.

Frishman *et al.* (*Ind. Eng. Chem.*, 1948, **40**, 2280) has investigated the action of chlorine on wool and found that at pH 1 there resulted a loss in weight and destruction of the surface scale structure ; pH 3–7, there was considerable modification of the fibre in that the cystine content was reduced and the solubility in alkali solutions greatly increased ; pH 9–11, only minor changes in the wool protein occurred.   Incidentally, wool treated with hypochlorite solutions at pH 8–9 may, with the minimum of fibre modification, be rendered resistant to shrinking.

Ridge and Little (*J. Text. Inst.*, 1942, **33**, T 33, 39) emphasise the need for controlling the pH of alkaline hypochlorite solutions for, otherwise, hydrochloric acid is set free with a consequent fall in pH and unsatisfactory bleaching may result.

A continuous wool bleaching process has been patented by Alexander, Earland and Wolsey Ltd. (B.P. 637,150, 1950) by which the wool is padded in a dilute aqueous solution of hydrogen peroxide at pH 6–11 at not more than 50° C. until the wool is thoroughly wetted.   The excess of the solution is then run off and the wool is heated to 70–100° C., though heating for 1½ hours at 85° gives the maximum whiteness.

Korte and W. Kaufmann (*Textilber.*, 1942, **23**, 234) claim that sodium chlorite at pH 3–6 is to be preferred to either sodium hypochlorite or hydrogen peroxide with fabrics that are difficult to bleach or are easily degraded.   A powerful bleaching agent, which operates at pH 7·0–8·2 (which is lower than that required for hypochlorite) is sodium hypobromite (Bloch *et al.*, ·*Textilber.*, 1948, **29**, 57, 96, 133 ; B.P. 615,604).

The possibility of photochemical decomposition is an important factor in the life of silk goods.   Harris and Jessup (*Bur. Stand., J. Res.*, 1931, **7**, 1179) find that the maximum resistance to light is provided at pH 10, and they suggest that the object of commercial finishing processes should be to leave the silk with a pH of about 10.   Another point of technical

importance is the production of silk which has the maximum
electrical resistance. Denham, Huttón and Lonsdale (*Trans.
Faraday Soc.*, 1935, **31**, 511) find that this condition is reached
by immersing degummed mulberry silk in a buffer-solution at
pH 4·2. This point lies between pH 3·8 and pH 4·7 at which
silk filaments undergo minimal swellings.

Most work appears to have been directed to dyeing operations,
which, in the case of the protein bodies contained in wool and
silk, involve mainly chemical combinations between acidic and
basic groupings. The quantity of an acid dye adsorbed by a
protein appears from the work of Chapman, Greenberg and
Schmidt (*J. Biol. Chem.*, 1927, **72**, 707) to be proportional to
the amounts of its basic components, *viz.*, arginine, histidine,
lysine. They were unable to obtain any evidence of physical
adsorption between pH 2·5 and 1·0. The dyeing of wool has
been investigated by Briggs and Bull (*J. Physical Chem.*, 1922,
26, 845), Reinmuth and Gordon (*Ind. Eng. Chem.*, 1923, **15**,
818), and by Elöd and Pieper (*Z. angew. Chem.*, 1928, **41**, 16;
Trans. Faraday Soc., 1933, **29**, 327). Wool at pH 2 takes up
twice the amount of Crocein Orange as it does at pH 5, which is
within the isoelectric pH range. The behaviour of Crystal Violet
when applied to wool in liquors of initial pH values ranging
from pH 1 to 12 is typical of that of many basic dyes. The
absorption steadily approaches a maximum value from a solution
at pH 10. That enhanced dye-absorption should occur within
the alkaline range is in accord with the functioning of the acidic
groups of the protein molecule. A constant absorption of dye
took place in the vicinity of the isoelectric range, from pH 4·07
to 5·75. Ultramicroscopic examination afforded an explanation
of the unexpected maximum absorption at pH 10, in that it
showed that the dye particles then underwent an appreciable
increase in size, thereby impeding the dye penetration. Simi-
larly the adsorption of acid dyes decreases rapidly when the pH of
the dye solution exceeds the isoelectric point. The fact that
a basic dye is adsorbed at all by wool or silk when they are
behaving as bases, *i.e.*, at pH values less than pH 4·6, and that an
acidic dye is taken up at higher pH values, when the acid nature
is prevailing, may be due either to (*a*) the great insolubility of dye
(basic)—protein (acid) or dye (acid)—protein (basic) complexes,
or to (*b*) physical adsorption. Substances used in " weight-
ing " silk have marked effects upon the amounts of dye absorbed
and the pH values which are conducive to the most efficient
absorption.

Acid dyes on wool bleed to an appreciable extent, if the dye-

bath has a pH higher than 8·2. This fact is considered by Goodall (*J. Soc. Dyers and Colourists*, 1935, **51**, 211) to be caused by the resulting swelling of the wool fibre. He recommends the buffering of the dye solution at pH 8·2 by means of phosphate buffer.

The problem of dye fixation and mordanting has been studied by Lorenz and Michael (*Z. physikal. Chem.*, 1928, **137**, 142) from the standpoint of the Donnan Membrane Equilibrium. They found that the optimum pH for absorption from given concentrations of dyestuff agree closely with those calculated from the Donnan Theory. Mullin (*Tiba*, 1929, **7**, 853, 981, 1101, 1229, 1331, 1359; *Thesis*, 1929, Nancy) has devoted much attention to the importance of pH in the dyeing of viscose and cotton. The uniform dyeing of viscose is largely determined by the reaction of the fibres, in other words by the preliminary treatments such as scouring, desulphuring and neutralising. A moderately alkaline dye bath is preferred, buffered at, or just below, a pH, at which maximum dye absorption has previously been found to occur by the same fabric. This optimum pH varies with the kind of material. The pH of the rinsing water has been found to have some effect on the fastness of the dye to light. Another factor which in some instances may affect the fastness of the dyestuff is perspiration. McSwiney (*J. Text. Inst.*, 1929, **20**, 65P) gives as its pH range 5·1–6·8.

The importance of hydrogen-ion concentration in the application of dyes to mordanted fabrics, such as cotton, will be apparent from Table 226A in which data are reproduced from a paper by Marker and Gordon (*Ind. Eng. Chem.*, 1923, **14**, 818) concerning the absorption of acidic and basic dyes by hydrated alumina.

It will be seen from page 70 that aluminium hydroxide behaves as a base below pH 4, and assumes the nature of an acid above pH 8. The table shows that while there occurred some absorption of methylene blue and crystal violet from the acid solutions which were below pH 4, the absorption became very pronounced with increasing pH values. Using the acidic dyes, absorption was greatest from solutions of low pH. Moreover, it was observed that the regulation of the hydrogen-ion concentration had a marked effect on the colour fastness.

Hydrogen-ion concentration has an important influence on the colours produced by various dyestuffs. Holmes and Berliner (*Amer. Dyestuffs Reporter*, 1927, **16**, 81) have investigated the colours set up in different buffer solutions of known pH values, and have compiled a colour chart for use in the identification of dyes by the colours they give at different pH values.

TABLE 226A[6]

ABSORPTION OF ACIDIC AND BASIC DYES BY ALUMINA
(mg. Dye per 1 gram of Dry Gel)

Basic Dyes.				Acidic Dyes.			
Methylene Blue.		Crystal Violet.		Orange II.		Metanil Yellow.	
pH.	Mg.	pH.	Mg.	pH.	Mg.	pH.	Mg.
1·96	65·6	1·50	3	2·30	452	1·92	703
2·23	66·1	5·44	8	3·20	186	2·30	406
5·95	67·5	9·18	45	5·27	179	7·46	276
9·85	77·0	10·70	282	10·14	162	9·67	226
11·12	82·7	11·12	413	11·02	136	11·60	115
12·00	279·0	—	—	—	—	—	—

In all probability, pH control will find a place in the manufacture of azo-dyes, and also in dyeing processes in which they are developed on the fibre by diazotising and coupling. It is known that the hydrogen-ion concentration of the coupling bath is an important factor in the control of coupling, as it provides a method which materially assists in the reproduction of desired shades of colour and also in effecting a more complete coupling of the components. Thus Conant and Pratt (*J. Amer. Chem. Soc.*, 1926, **48**, 2468) showed that the coupling of five different diazonium salts with a variety of phenols and naphthols takes the form of a bimolecular reaction, the velocity constant of which is a function of the pH of the medium. A serious difficulty, however, is the inapplicability of the ordinary methods of determining pH values of these solutions, though it is possible, as Mullin has suggested, that glass electrode will be found of service. Cellulose acetate silk enters into combination with organic bases, *e.g.*, paranitraniline, benzidine, etc., which are diazotised on the fibre and then coupled with suitable naphthols and phenols to give various colours. After converting the dyestuffs into water-soluble hydrochlorides, the baths are neutralised with sodium hydroxide so as to liberate the free dye base in colloidal suspension, some of which becomes fixed' by the fibre. When the hydrochlorides alone are used, not only are the colours different, but the dye is usually badly fixed to the fibre. pH control of the neutralisation should result in the production of more satisfactory dyeing. The application of these dyes to cotton, for which the process is reversed by first soaking the cotton in the hydroxy-compound, lends itself to pH control.

As equilibria between acids and bases play a part in the application to acetate silk of the " dispersol dyes " and the S.R.A. dyes (in which water-insoluble basic dyes are dissolved in concentrated Sulpho-Ricinoleic Acid, or highly sulphonated castor oil), it is likely that the hydrogen-ion concentration of the dyebath is a factor of some importance, both as regards the dye fixation and
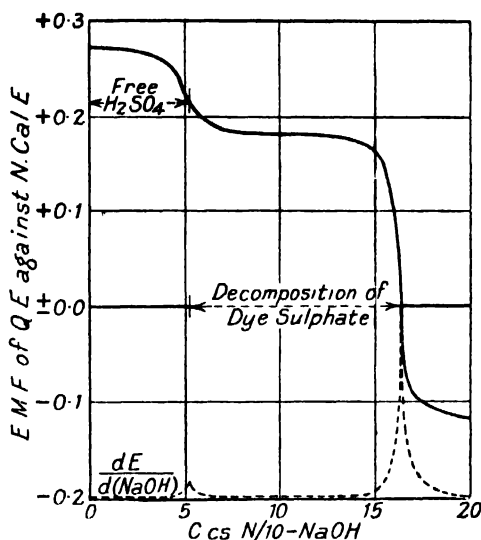
FIG. 191.—Quinhydrone Electrode Titration of a Dyestuff.

the possible deleterious effects on the acetate silk caused by hydrolysis through having too high a pH. The latter factor may arise in the laundering of acetate silk through the use of too alkaline a soap. Another point of importance in connexion with the use of sulphonated oils will be apparent from the work of Schindler and Schacherl (*Collegium*, 1930, 108), who found that strongly alkaline aqueous dispersions and dispersions of pH less than 4 underwent much hydrolysis. Highly sulphonated castor oil when boiled for half-an-hour at pH 4·2 was only slightly hydrolysed and remained intact at pH 6·8.

Potentiometric Methods for the Determination of Free Acid and Free Alkali in Dyestuffs.

Volumetric methods of estimating the acidity or alkalinity of dyestuffs are, of course, usually impossible. Callan and Horrobin (*J. Soc. Chem. Ind.*, 1928, **47**, 332T) have found the quinhydrone

electrode to be especially useful in finding the sodium carbonate content of Congo-red, Benzo-purpurine, Milling Yellow, Orange I, Rhodamine, and Brilliant Orange ; their results being in excellent agreement with those obtained by purely chemical methods. Since the quinhydrone electrode cannot be used in alkaline solution, they add a known amount of standard acid to a solution of a weighed amount of dyestuff, and after the carbon dioxide has been expelled by boiling, the cooled solution is titrated in the manner described on page 73, Vol. I. They find the method to be particularly applicable to the determination of acid in dye-stuffs and in dye-liquors, and to the detection of " free " acid in basic dyestuffs such as Brilliant Green, which is a hydro-chloride or sulphate of a colour base. Fig. 191 gives a quin-hydrone electrode titration curve of Brilliant Green sulphate, from which it will be seen that the amounts of free and combined sulphuric acid can be readily obtained. A modified form of Callan and Horrobin's method has been used by Bromley and Causer (*Analyst*, 1930, **55**, 277) in the determination of the acidity of writing inks.

Artificial Protein Fibres.

Careful pH control is necessary at various stages of the different processes of manufacturing artificial casein yarn. Thus the pH of the casein solution to be extruded should be between 5 and 7.

As examples of the kind of pH control that may be involved, brief reference will be made to two processes. In the one des-cribed by Peterson, McDowell and Hoover (*Text. Res. J.*, 1948, **18**, 744) the casein solution is set at pH 7. The solution is extruded into an acetic acid bath and, after stretching the tow 100 per cent. in an aluminium sulphate-formaldehyde bath, it is treated with a solution of sodium acetate at pH 6. Finally the product is acetylated.

In the method, originating from the Eastern Laboratories of the U.S. Department of Agriculture (*Chem. Eng. News*, 1950, **28**, 459), the casein solution is buffered at pH 6·5 and is extruded and spun in a sodium sulphate bath, adjusted to pH 3·5 with acetic acid. The casein tow is then treated under tension with a solu-tion containing aluminium sulphate, formaldehyde and sodium sulphate at pH 3. Afterwards it is stretched 300 per cent. in air, then held on rollers for treatment with sodium acetate solution at pH 6·0, and finally in a relaxed condition the yarn is rendered more insoluble by passing it through an acid formaldehyde solution.

According to Traill and McLean (*J. Soc. Chem. Ind.*, 1945, **64**,

221) the pH of the solutions in which spinning is carried out is important for they state that fibres spun at pH 10·4 are not as strong as those spun at pH 9·2 or pH 6·7.   The pH of the solutions in which hardening is effected seems also to be important.   Unlike the solutions described above, McMeekin, Reid, Warner and Jackson (*Ind. Eng. Chem.*, 1945, **37**, 685) used a two-per cent. formaldehyde solution at pH 4·7 for the manufacture of casein monofil fibres suitable for brush-making.

Permanent Waving of Hair.

Heilingotter (*Mfg. Chem.*, 1951, **22**, 224) has shown that thioglycollic acid, which is used for the permanent waving of hair, may be oxidised almost completely (99·5 per cent.) by adding 0·5 c.c. of a 30-per cent. hydrogen peroxide solution to 5 c.c. of solution at pH 9·4 ; at pH 7, 74 per cent. was oxidised in 1 minute, whereas at pH 4, 90 per cent. was oxidised in 6 minutes.

CHAPTER XLVII

ORE FLOTATION

CONSIDERABLE advances have recently been made in the development of flotation methods for the separation of ores from foreign matter, and also for the separation of one ore from another. The latter process is known as either differential, preferential, or selective flotation. After the minerals have been suitably ground, they are allowed to pass into a circuit of flowing liquid upon which some of the lighter and finely divided ores float, whereas the heavier and coarser particles sink. These methods have been extremely useful in ore concentration, especially in connexion with the sulphide ores, which when in similar states of subdivision are able to float to about the same extent. Notwithstanding this, it is very often possible to add some substance to the flotation medium that will cause the sulphide of some particular metal to sink. Thus at Cananea, Mexico (Tye, *Amer. Inst. Min. Met. Eng.*, 1927, Tech. Pub., No. 3) copper ore is extracted from a mineral, comprising chiefly chalcocite with some copper pyrites associated with iron pyrites in a siliceous gangue high in alumina, first by depressing the iron pyrites in alkaline circuit by means of as little as 0·08 lb. of xanthate per ton of ore. The concentrate contains only 4·6 per cent. of silica, which eliminates the need for roasting, and the concentrates are consequently placed in the reverberatory furnace. Because of the economic advantages accruing from these methods, their rate of development has been much greater than that of the chemistry and physics underlying them. The amounts of depressants to be added require careful control, and owing to the many and variable factors involved, such control is far from easy. When a satisfactory means of control has been devised, then it will be possible to obtain cleaner separations. Thus a varying proportion in an ore of the amount of a sulphide to be depressed will necessitate corresponding variations in the concentration of depressing agent in the flotation cells.

The mechanism of flotation is linked up with the operation of surface reactions, and therefore involves the following factors : size of particle, the angles of contact made between the particles and the liquid surface, the surface tension of the medium, adsorption at the surfaces of the particles, and the tendencies of the

particles to flocculate. Usually, the flotation medium is a mixture of water and oil. Flotation oils are both polar and non-polar. The former contain either alcohol- or carboxyl-groups which tend to make the oils soluble in water, and in the case of insoluble oils, to form extensive oil films on the surface of the water. This solubility influence of the polar groups becomes less and less as the chain of —CH_2 groups becomes longer. Hydrocarbons, containing no polar groups, therefore, have only very slight or no solubility and spread on water to very small extents.

Almost all derivatives of the paraffins and the aromatic compounds (*e.g.*, alcohols, aldehydes, and acids) lower the surface tension of water, and for this reason on dissolving in water they tend to concentrate in the surface layer. With insoluble oils containing polar groups the tendency to dissolve rests in the polar groups, and as Langmuir (*J. Amer. Chem. Soc.*, 1917, **39**, 1849) showed, in the surface layer of oil on water the polar groups arrange themselves in direct contact with the water surface, leaving the non-polar or inactive groups to find the remote positions. This tendency to dissolve results in a lowered surface tension, and moreover, through the possible supersaturation of the surface layer of the water, in the formation of foam. A non-polar oil, on account of its inability to diminish the surface tension, is not adsorbed in the surface layer, and therefore accumulates on the surface in lenticular globules.

It has been pointed out that oils become adsorbed by minerals with their polar ends drawn into immediate contact with the surfaces, so that their inactive non-polar ends are outermost and thus come into contact with the flotation medium. Provided the particle were sufficiently small, this non-polar coating would tend to keep the oil-coated particle (as is the case with a globule of non-polar oil), floating on the surface of the liquid by virtue of its surface tension. Any diminution in the magnitude of the surface tension of the liquid might cause the particle to sink.

Now Langmuir has found that films of various fatty acids, alcohols, and esters are extraordinarily sensitive to very small amounts of acid, but not to salts in any great measure. N. K. Adam (*Proc. Roy. Soc.*, 1921, **99A**, 336) confirmed these results for palmitic acid, and furthermore found that the properties of the oil film on the surface of the water underwent variation with change in hydrogen-ion concentration. Though the films are insoluble in acid solution they become increasingly soluble with increasing *p*H, through the formation of salts. It will be seen therefrom that the *p*H of the medium may be expected to have an important

effect on its surface tension, and therefôre upon its ability to float mineral particles.

Substances used as flotation promoters and depressants materially affect the hydrogen-ion concentration. To cause flotation of a mineral, acids are often employed, *e.g.*, sulphuric acid. Other substances used in flotation work are sodium carbonate, disodium phosphate, sodium cyanide, potassium bichromate, and copper sulphate. In differential flotation disodium phosphate is extensively used. Mineral suspensions appear to increase in stability in solutions having a *p*H greater than 7, and to show a tendency to flocculate in acid media. Fahrenwald (*Trans. Amer. Inst. Min. Eng.*, 1924, **70**, 647) states that, in general, hydrogen-ion concentration appears to be *the* important factor in regard to the magnitude and sign of an electric charge on mineral suspensions. Sufficient has been written to indicate the possibilities of hydrogen-ion concentration control, though control will also depend upon many other factors inherent in flotation processes. (For further information, the reader is referred to Technical Publications, Nos. 3 to 5, of the American Institution of Mining Engineers, 1927 and Wark and Cox, *Tech. Publ.*, No. 495, 1933).

Gaudin (*Min. and Met.*, 1929, **10**, 19) has investigated the effect of *p*H variations in a flotation pulp containing xanthates. Chalcocite may be completely recovered within the range *p*H 1–12, whilst pyrite tends to sink at *p*H values higher than 6·2. By means of amyl xanthate within the range *p*H 9–11, malachite, free from calcite, may be floated. By using oleic acid and copper sulphate, felspar may be made to float completely on solutions of *p*H 6·5–10. Copper sulphate has a marked effect on the flotation of quartz between *p*H 6 and 11, whilst in a small amount in the presence of xanthates it activates zinc blende in acid circuit, and when in a large amount blende may be made to float in both acid and alkaline media.

An 80 per cent. recovery of gold and silver may be obtained from an oxidised copper ore containing jasperised quartz by flotation at *p*H 6 with sodium ethylxanthate and dixanthogen-6 using pine oil as the frother. (Laschinger, *J. Chem. Met. Soc.*, S. Africa, 1937, **38**, 225.)

The *p*H value influences the adsorption of amines by minerals. Wark and Wark (*J. Physical Chem.*, 1935, **39**, 1021) find that with 50 mg. of hexylamine per litre at *p*H 10·5 sphalerite can be floated away from galena, the hexylamine serving both as collector and frother. Similarly very finely divided chalcocite can be floated away from galena using either amyl dixanthogen or potassium amyl xanthate (Malozemoff, *ibid.*, p. 1043).

CHAPTER ·XLVIII

1. Manufacture of Sweets.

THE character of syrups used in the confectionery industry is partly determined by the hydrogen-ion concentration during the boiling process, inasmuch as it is a factor on which the activity of invertase depends. The optimum pH value is about 4·5, a point that should be considered in the production of golden syrup, corn syrup, cane and sorghum syrup, and maple syrup. The inversion of cane sugar during boiling with acids is proportional to the hydrogen-ion concentration. If the extent of inversion has been too great the syrup will be unsuitable for making into hard sweets. Advantage is taken of the action of invertase in preparing fondants and the creams, whose consistencies are the direct result of the proportion of glucose formed. It is probable that pH measurements would furnish a method of control.

According to Grewe (*Cereal Chem.*, 1930, **7**, 59) the colour-producing constituent of chocolate has the properties of an indi- • cator, being yellow at pH 5·0 and red at pH 7·5. A rich mahogany colour can be imparted by raising the pH to 8·0 by including a little sodium bicarbonate, which has no detrimental effects on the flavour. For this reason fresh milk when used in making milk-chocolate gives a dark cake whilst sour milk produces a much lighter cake. The precise colours obtained, however, also depend on the quality of the chocolate used.

2. Preservation and Canning of Food Products.

In order to preserve grain from possible diastatic action on the starch from split grains, Legendre (*Comp. rend.*, 1927, **185**, 1156) recommends the addition of small quantities of alkali materials to raise the pH. The absence of sugars, caused thereby, prevents further bacterial action, and so eliminates the usual rise in temperature during the storage of grain with the attendant troubles of germination and fermentation.

In the pasteurisation of fruit juices, yeasts and moulds must be destroyed, though the destruction of many kinds of bacteria is unnecessary. Two points must be considered : (1) the rate of

killing the destructive micro-organisms, and (2) the rate of the penetration of heat.   In the destruction of micro-organisms the pH value is of vital importance, though this varies in the case of different bacilli.   The mould, *Byssochlamys fulva*, is heat-resistant and causes the disintegration of canned fruits.   Its resistance to heat is greatest at pH 5, whilst it is less resistant at pH 7 than at pH 3 (*Fruit and Veg. Pres. Res. Sta., Campden, Ann. Rept.*, 1936–7).   Notwithstanding this, it is highly desirable to maintain in canned fruit a pH value equal to that in the ripe fruit in view of the possible influence on the taste that may be introduced by a variation of this factor.   Other difficulties arise in canning through corrosion caused by the natural acidity of the products.   The pH of fruits lie below 4, tomatoes about pH 4·2, vegetables usually between pH 5 and 6, and protein foods, *e.g.*, peas, fish, and meat, between pH 6 and 7 (*cf. National Canners Assoc., U.S.A., Bull.* 17L).   Table 227 gives the pH values and titratable acidities, calculated as percentage of citric acid, of canned fruits.   The data enclosed in brackets represent average values.   The table is taken from the Annual Report, 1935–6, Fruit and Vegetable Preservation Research Station, Campden, University of Bristol.

Observations by Kohman and Sandborn (*Ind. Eng. Chem.*, 1930, **22**, 615) on the effects of fruits on the tinned iron used in cans, show that tin tends to become anodic with regard to iron , with decreasing pH there is a greater tendency for enamelled tinned-iron cans to swell, through the development of hydrogen, and to perforate, owing to the ease with which any exposed tin becomes dissolved.   They attribute this enhanced tendency to the anodic action, being confined to very small areas which thus exposes the iron to the corrosive action of the fruit juices.

Using a 0·5–1 per cent. solution of citric acid containing varying amounts of sodium citrate to give pH values ranging from 2·4 to 5·5, Morris and Bryan (*D.S.I.R Food Invest. Spec. Rep.*, No. 44, 1937) found that, in the absence of air, the tin in tin-iron couples and in tin plate becomes increasingly corroded as the pH is raised from 2 to 4, while the corrosion of the iron diminishes. Admission of air increases the corrosion of tin, especially at low pH.   Regarding the storage of· dehydrated prunes in syrup, Kohman and Sanborn (*Ind. Eng. Chem.*, 1933, **25**, 920) state that the pH of the syrup is about 4·0.   This causes appreciable corrosion of tin-iron cans, but these workers find that the insertion of sufficient ·citric acid or lemon juice to give pH 3·8 eliminates corrosion without materially affecting the flavour of the prunes.

Mild steel is appreciably corroded by solutions of low pH.

* TABLE 227

pH AND TITRATABLE ACIDITIES OF ENGLISH (I) AND FOREIGN (II) CANNED FRUITS

		pH.	Per cent. Titratable Acidity (as Citric Acid.
I.	Plums, purple	2·69–2·89 (2·79)	1·09–1·36 (1·25)
	,, golden	2·80–3·09 (2·93)	0·88–1·10 (1·01)
	,, Victoria	2·83–3·07 (2·95)	0·62–0·85 (0·76)
	Damsons	2·91–3·16 (3·02)	1·11–1·59 (1·39)
	Greengages	2·96–3·36 (3·17)	0·62–0·97 (0·78)
	Apples (solid pack)	2·84–3·14 (2·96)	0·44–0·97 (0·68)
	Cherries, acid	3·03–3·39 (3·23)	0·61–1·14 (0·86)
	,, sub-acid	3·24–3·34 (3·30)	0·76–0·85 (0·80)
	,, sweet	3·63–4·31 (3·86)	0·16–0·35 (0·25)
	Gooseberries	2·72–3·16 (2·96)	0·97–1·43 (1·15)
	Blackberries	2·81–3·40 (3·02)	0·70–1·40 (1·03)
	Strawberries	3·16–3·76 (3·46)	0·38–0·71 (0·47)
	Raspberries	2·78–3·46 (3·05)	— (0·83)
	Blackcurrants	2·82–3·47 (3·10)	1·30–2·02 (1·64)
II.	Grapefruit	3·16–3·49	0·61–1·35
	Bilberries	3·00–3·60	—
	Peaches	3·43–3·91	—
	Apricots	3·51–3·79	—
	Pears	3·62–4·33	—
	Pine-apples	3·41–4·30	0·21–0·75
	Muscat grapes	3·44–3·76	0·20–0·36
	Quinces	3·34	0·39
	Cape berries	3·76–3·86	0·88–0·97
	Mandarin oranges	3·80–3·84	0·55–0·58
	Nectarines	3·96–4·07	0·20–0·37
	Guavas	3·98–4·28	0·19–0·33
	Mangoes	3·43–4·69	0·12–0·61
	Litchis	4·09–4·39	0·20–0·29
	Tomatoes	4·38–4·56	0·30–0·50
	Rambutano	4·78–4·81	0·19–0·20
	Papaws	4·68–5·21	0·03–0·07
	Loquats	4·93–5·36	0·01–0·02
	Figs, fresh	5·17	0·39

Morris and Bryan (*Trans. Faraday Soc.*, 1933, **29**, 398), however, found that the presence of tin salts in the form of citrates reduces the corrosion considerably. Above pH 4, much hydrogen may be evolved as the result of corrosion. Bryan (*ibid.*, 1933, **29**, 830) confirmed the greater corrosion of iron at pH 5 than at pH 3.

Although pH is undoubtedly an important factor in causing tin to dissolve in the syrups of tinned fruits, it is not the prime factor, for there is no direct correlation between the pH and the quantity of tin which dissolves. (Adam and Horner, *J. Soc. Chem. Ind.*, 1937, **56**, 329T). Vegetables, pH 5·0–6·3, often attack tin more severely than do fruits. This might be caused by the formation of soluble complex compounds with the amino-acids in the vegetables. Asparagus, dwarf beans and spinach all tend to produce corrosion.

Of the dyes, Erythrosin, Ponceau 3R and Amaranth, used in dyeing cherries, Jeffrey and Cruess (*Ind. Eng. Chem.*, 1929, **21**, 1268) find that dyeing with Erythrosin is most amenable to pH control. The dye is best applied in a sodium bicarbonate solution at pH 7·5 and fixed at pH 3·0–3·5 by means of citric or other permissible fruit acid.

3. Honey.

The activity of honey diastase is greatly affected by pH ; the maximum activity being reached at about pH 5·3 (Lothrop and Paine, *Ind. Eng. Chem.*, 1931, **23**, 71 ; Schuette and Pauly, *Ind. Eng. Chem., Anal. Edn.*, 1933, **5**, 53). Lampitt, Hughes and Rooke (*Analyst*, 1930, **55**, 666) find that the optimum pH for amylase activity is 5·0–5·3 at any temperature.

Coagulation of honey colloids takes place at their isoelectric point, pH 4·3 (Lothrop and Paine, *Ind. Eng. Chem.*, 1931, **23**, 328).

4. Pectin, Jam and Fruit Jellies.

Pectins are polysaccharoses, which are present in many fruits : apples, plums, pears, grapes, citrus fruits ; in many vegetables : carrots, turnips, beans, sugar beet ; in many fruit seeds : plum, orange and grape-fruit seeds ; and in the tissues of many plants. In general, the pectin content of fruits increases during the ripening process and, once the fruit is ripe, the pectin begins to diminish in amount. Pectin is a methoxy ester of pectic acid, which contains 11·76 per cent. of methyl alcohol, pectic acid being a complex galacturonic acid combined with arabinose and galactose (*vide* Branfoot, *Food Invest. Board, D.S.I.R.*, No. 33, 1929). The pectins are responsible for the formation of jelly in jams and in fruit jellies.

Pectin is manufactured from beet sugar residues and from apple and other fruit pulp. One method, that of Poore, is to filter the aqueous pectin extract through kieselguhr, precipitate with 95 per cent. alcohol, and then add enough absolute alcohol to convert the precipitate into a thick paste. The paste is kneaded and the alcohol is removed by pressing. The process is carried out at 68°, and is repeated several times. The pectin so purified, is dissolved in water for use.

The jelly strength of apple pectin gels depends, according to Olsen (*J. Physical Chem.*, 1934, **38**, 919), on (*a*) the concentration of sugar, (*b*) the pH, (*c*) the time of heating and (*d*) the temperature at which heating is carried out. With 70 per cent. of sugar, the maximum jelly strength is established at pH 3·4 ;

with 60 per cent., at pII 2·9 and with 55 per cent., at pII 2·5. Similar observations were made by him (*Ind. Eng. Chem.*, 1933, **25**, 699), using citrus pectin. The pH for gelation is in the vicinity of 3. Stuewer, Beach and Olsen (*ibid.*, 1934, **6**, 143) found that treatment of apple pectins with lactic acid or tartaric acid causes gelation at pH 2·55.

Lampitt and Money (*J. Soc. Chem. Ind.*, 1937, **56**, 290T) have shown that the jelly strength increases rapidly as the pII is lowered to 3·0, and then more slowly as the pII is decreased from 3·0 to 1·0. It appears to be immaterial, as far as jelly-strength is concerned, whether citric acid or hydrochloric acid be used to lower the pH.

Certain enzyme preparations are available for the hydrolysis of the starch present in pectic extracts from apple pomace. Baker and Kneeland (*Ind. Eng. Chem.*, 1935, **27**, 92) point out that these preparations contain the enzyme, pectinase, which promotes the hydrolysis of pectin itself, and so diminishes the viscosity of the pectin solution. This occurs particularly at pH 3·3–5·0 at 40°, so that if such preparations are used, care should be taken to maintain the pH at 3·3 or lower, at which pH the activity of the pectinase is considerably reduced.

In the manufacture of fruit jellies and jam, the pectin contents of the fruits should be known so that, in the case of fruits, containing an inadequate supply of pectin, the deficiency can be rectified ; the pH and buffer capacity of the fruits should also be known. In cases where insufficient natural acid is available, then acid should be introduced to reach a pH which will ensure a suitable jelly strength. Fruits low in pectic materials are rhubarb, apricots, strawberries, pineapples, cherries. Fruits, which contain too little acid, are strawberries, cherries, sweet apples, pears, peaches, melons and figs, and to which acid must therefore be added. Prolonged boiling causes the pectic decomposition of the pectin and caramelisation of the sugar. Another point concerns the use of over-ripe fruit or unsound fruit. In both instances, pectin decomposition has already begun, which is hastened by heating.

Myers and Baker at the Delaware Agriculture Experimental Station (*Bulls*. Nos. 141 and 144, 1926) studied the effect of the pII values of fruit juices used in the manufacture of jellies. At pH's above pII 3·50 to 3·55 it was not possible to prepare jellies. The most suitable pII range for the preparation of jellies appears to be from pH 2·85 to 3·30, the precise reaction depending on the nature of the acid used and the salts present.

5. Meat.

As soon as a normal animal is killed and rigor mortis sets in, lactic acid is developed in the muscles to the extent of 0·7–1·0 per cent. Beef develops about 0·9 per cent. of lactic acid during the first 30 hours after slaughter when the temperature falls from 37° to 21° C. (*D.S.I.R., Food Invest. Spec. Rept.*, No. 36). Lactic acid is also developed and tenderness improved when beef is hung for two to four days. These points are of importance in meat canning and also in the manufacture of meat extracts, the soup being easier to concentrate. This increase in lactic acid content is reflected in a fall of pII.

The amount of drip from frozen meat on thawing seems to have some connexion with the pH of the meat. Empey (*J. Soc. Chem. Ind.*, 1933, **52**, 230T) obtained pII values ranging from 5·42 to 6·53 for the semimembranosus muscle of beef after the completion of rigor mortis. He concluded that some correlation exists between the pH and the amount of drip. The amount of drip appears to be at a minimum from meat at pH 6·3 and increases with falling pII. Similar observations were made by Sair and Cook (*Canad. J. Res.*, 1938, **16**, D, 255), who state that drip is at a maximum from beef at pH 5·2–5·5 and ceases altogether at pH 6·4.

A high pII is usually to be associated with the incidence of putrefaction. This has been found to be the case with beef, horseflesh, pork and fish. Thus Herzner and Mann (*Z. Unters. Lebensm.*, 1926, **52**, 215) and Strohecker, Vaubel and Kirchberg (*Z. anal. Chem.*, 1937, **110**, 1) find that beef is definitely tainted when the pII is above 6·3. The pII of fresh beef is 6·16–6·20. Schmidt (*Arch. Hyg.*, 1928, **100**, 377) states that at pII 6·3 horseflesh has become spoiled. The pII of pork, according to Sair and Cook, is somewhat variable between 5·6 and 6·3, and Callow (*Food Invest. Board, D.S.I.R. Rept.*, 1937, p. 49) finds that a high pII affords a real indication that matured hams have undergone bacterial spoilage. Strohecker *et al.* give pH 6·68–7·34 for fresh fish (cod, salmon and haddock), and point out that putrefaction has begun when the pH has risen above 7·5.

Smith (*Food Invest. Board Rept.*, 1937, 24) finds that ox-muscle, taken from the vicinity of the hip-joint, is apt to be covered with synovial fluid. Whereas the pII of ox-muscle is usually below 6, that of synovial fluid is 7–8, which happens to be the optimal range for many bacteria which cause putrefaction. There is thus a tendency for such cuts of beef to become tainted. In regard to the fatty tissue and muscle of the pig, Lea (*J. Soc. Chem. Ind.*, 1937, **56**, 376T) finds that they contain an enzymic

system—lipoxidase, which promotes oxidation and rancidity in fat. The activity of the enzyme is high between pH 4 and 5 and falls considerably at pH values above 6.

The curing of meat with sodium nitrite has been investigated by Duisberg and Miller (*Food Res.*, 1943, **8**, 78) who found that owing to the instability of nitrous acid below pH 4·4 the fixation of the colour in pork is negligible. Between pH 4·4 and 5·0 the colour fixation is negligible although some nitrite may be present, but between pH 5·0 and 7·0 it is satisfactory. Above pH 7·0 the pork becomes undesirably soft.

The mode of treating comestibles by quick-freezing may, according to Taylor (B.P. 311,317/1929), be improved by immersion in brine, to prevent the subsequent absorption of water from the buffer, and then in a buffer-solution at pH 7 in order to prevent drip on thawing.

Regarding the storage of preserved meat in aluminium containers, Bidault and Blaignan (*Rev. hyg. méd. prév.* 1930, **52**, 122) found that meat broths, varying from pH 4·5–8·0, dissolved in eight months amounts of aluminium that ranged from 0–0·0145 gram per 100 grams.

Among canned meats, tripe is particularly subject to ferrous sulphide discoloration, the iron probably coming from the joints of the tin-plate cans. Rupp (*Ind. Eng. Chem.*, 1935, **27**, 1053) suggests that by keeping the pH of the tripe at 5·6, the concentration of hydrogen ions is then sufficient to repress the ionisation of the dissolved hydrogen sulphide, originating from the tripe, such that, even with the slightly increased concentration of ferrous ions, introduced through the low pH, the precipitation of ferrous sulphide on the tripe is avoided.

6. Insulin.

The range of precipitation of normal insulin is pH 4·2 to a little above pH 7, the maximum occurring at pH 5·4, the isoelectric point (Howitt and Prideaux, *Proc. Roy. Soc.*, 1932, B, **112**, 13 ; Harvey, Howitt and Prideaux, *Trans. Faraday Soc.*, 1924, **30**, 407).

7. Lead Chromate Pigments.

Precipitation at pH 3·5 yields a yellow lead chromate. Above pH 9, depending on the precise pH, various orange shades may be obtained (Ernst and Snyder, *Ind. Eng. Chem.*, 1932, **24**, 227 ; Ernst, Pragoff and Litkenhous, *Ind. Eng. Chem.*, *Anal. Edn.*, 1931, **3**, 174).

8.　Photography.

The many papers which have been published by Sheppard and his collaborators of the Kodak laboratories during the last few years emphasise the value of pH control.　Thus hydrogen-ion concentration has an important effect in the formation of emulsions and on the size of the silver halide particles dispersed within them.　The tanning action, or "hardening," of aluminium or chromium salts on the gelatin emulsion is dependent upon acidity. Neutral salts also exercise a temporary "hardening" action, and this likewise is a function of pH.　Undue swelling of the gelatin film is prevented by the use of such solutions which, through their "buffer action," maintain a suitable range of pH.　A point in connexion with the ampholytic nature of gelatin is that, unless its pH value is controlled, the film may, in undergoing hydrolysis, cause the reduction of the silver salts.　The reducing action of organic developers, *e.g.*, hydroquinone, is determined, not only by their concentrations in the reduced and oxidised forms, but by the hydrogen-ion concentration (*cf.* p. 2).　This has been proved to be the case with "elon" (p-methylamino-phenol sulphate) by Cameron (*J. Physical Chem.*, 1938, **42**, 1217), who has shown that the "redox" potentials can be explained in terms of the ratio of reduced and oxidised forms, the pH and the various basic and acidic dissociation constants involved (see also Fieser, *J. Amer. Chem. Soc.*, 1930, **52**, 4915, 5204; 1934, **56**, 1565; 1935, **57**, 491).　The reactions of agents employed in sensitisation, and especially of certain dyes, used for compensating optical defects, are influenced by the prevailing pH. Another point of interest concerns the "hypo" fixing bath.　If the pH of the bath falls below about 3·5, the thiosulphate decomposes with the separation of finely divided sulphur, whereas if any iron compounds are present they will undergo precipitation with the production of stains when the pH exceeds about 5·5. (See also Rawling, *Phot. J.*, 1929, **69**, 83; Tritton, *ibid.*, p. 281; Steigmann, *Phot. Ind.*, 1934, **32**, 93; Reinders and Beukers, *Ber. int. Kongr. wiss. angew. Phot.*, 1931, **8**, 171.)

According to Weyerts, Wiedenhold and Kodak Ltd., B.P. 542,507, polyvinyl phthalate may be used to increase and control the viscosity of gelatin solutions or photographic emulsions. By maintaining the pH of the resin-gelatin solution between 5·5 and 6·5 there is little change in viscosity and the photographic properties of the emulsions are not affected by the inclusion of the synthetic resin.

9. Emulsions.

Emulsification of oil-water and tar-water mixtures is often effected with the aid of emulsifying agents, such as gums and soaps, and the emulsions so formed are stabilised by the inclusion of small proportions of acid or alkali. The stabilising action is probably due to the chemical combination which takes place with the emulsifier, and to the effect which this combination has in reducing the interfacial tension at the oil-water surfaces. In the past there has been a tendency to attribute variations in the stability of an emulsion to specific ions, and to overlook the fact that the salt solutions containing these ions may have materially altered the pH of the emulsion.

Krantz and Gordon (*J. Amer. Pharm. Assoc.*, 1926, **15**, 83) prepared 25 per cent. emulsions of cotton-seed oil and water and of heavy mineral oil and water, using acacia and tragacanth as emulsifiers, and studied the effects on their stability introduced by variations in pH values obtained by adding different amounts of sodium hydroxide and hydrochloric acid. The range of greatest stability for the emulsions of either vegetable or mineral oils prepared with acacia lay between pH 2 and 10, whereas using tragacanth, the emulsions were only stable over the range pH 1·9 to 2·3. The size of the particles in the acacia emulsions were far more uniform and smaller than those in the tragacanth emulsions, and with the former there was a slight increase in the particle size on both the acid and alkaline side of the pH range, due to coalescence prior to the actual separation. The tragacanth emulsions were especially stable within the narrow pH range indicated, but quickly separated at higher pH values. The formation of water-in-oil emulsions with the aid of magnesium oleate was found to be more satisfactory in the case of olive oil than of mineral oil. The pH range of maximum stability was from 11 to 12·5, and when the pH fell below 2·5 extreme instability was produced (see *Colloid Symposium Monograph*, VI., 1928, pp. 173 to 206 ; Krantz, *J. Amer. Pharm. Assoc.*, 1930, **19**, 1181). The most satisfactory emulsions of vegetable oils, *e.g.*, olive oil, in water, according to Travis (*Ind. Eng. Chem.*, 1931, **21**, 421), are obtained by adding a little oleic acid and 0·25 per cent. of gum karaya and adjusting to pH 8 by adding sodium hydroxide.

Tar emulsions in water suitable for road spraying, may be prepared with the aid of soap and the adjustment of pH.

10. Soap and Bath Salts.

Ordinary soaps impart to water a pronounced alkaline reaction, varying as a rule from about pH 10 to pH 11·5. This high pH

accounts for the precipitating action of soap on the magnesium and calcium salts contained in the water, the precipitate consisting chiefly of magnesium and calcium soaps.

It is due to such high pH's that soaps have sometimes an irritating effect on the skin ; they dissolve out the natural fatty sebaceous secretions deposited on the skin and so rob it of its protective layer. Nevertheless, it is necessary to remove the matter deposited from the sweat glands in the pores. Among the substances used as bath salts are sodium carbonate, borax and disodium phosphate, of which the first sets up the higher pH and the latter the lower. Except for its slower rate of dissolution, borax has advantages in that it produces a pH value of about 9, which undergoes very little change with dilution, and does not precipitate as much of the salts as does sodium phosphate.

The pH of borax solutions varying from 0·2 to 9 per cent. ranges from 9·2 to 9·3 at 18°, and from pH 8·9 to 9·0 at 60° C. Borax, when used with a good quality soap, considerably reduces the alkalinity of the soap. Thus at 38° to 40° C. a 0·5 per cent. borax solution had a pH value of 9·1, whereas a 5 per cent. toilet soap solution had a pH value of 10·3, yet the same amount of soap dissolved in a 0·5 per cent. borax solution yielded a solution of pH 8·8.

The factors governing the detergent action of soap solutions appear to be (a) hydrolysis of the soap, (b) variations in surface tension, and (c) foam formation. Thus detergency seems to be greatest when the surface tension of the solution has been rendered as small as possible, which is also the condition for the volume of the foam formed to be at a maximum. These properties are intimately connected with the hydrolysis of the soap, the extent of which can be varied by the use of " builders."

As the detergent action of soap solutions is determined by a combination of several variable factors, it becomes apparent that pH control of soap solutions employed will be of real assistance only when the laundering is carried out with solutions of known concentration and under standardised conditions.

" Builders " are salts, which, owing to their hydrolysis, impart to the solution a high pH, e.g., sodium silicates, $2Na_2O,SiO_2$ and Na_2O,SiO_2, sodium orthophosphate and sodium carbonate. The anions may also have an important influence on the laundering efficiency of the soap. Rhodes and Bascom (*Ind. Eng. Chem.*, 1931, **23**, 778) find that the maximum detergent action of soap is attained at pH 10·7, but that the actual increase in the detergent power depends, to a marked extent, on the anions present in the builder, whilst Snell (*ibid.*, 1932, **24**, 76) states that the

builder should set up a buffer action above pH 10 and he considers $2Na_2O,SiO_2$ to be the most suitable for the purpose, although sodium metasilicate is very effective (see also Rhodes and Wynn, *ibid.*, 1937, **29**, 55). Baker (*ibid.*, 1931, **23**, 1025) has measured the volume of foam produced when alkali and " builders " are added to soap solutions to set up various pH values. In every case there is an increase to maximal values, which as the pH is still further increased, the volume of foam produced undergoes a very rapid diminution. Sodium metasilicate was the most effective and gave a maximal volume of foam at pH 12–13. Sodium hydroxide alone was not so effective but gave a maximum between pH 12 and 13. Sodium orthophosphate gave a maximum foam between pH 11 and 12 and sodium carbonate at pH 11. When builders are used the subsequent need for neutralisation arises. Snell (*ibid.*, 1937, **29**, 560) points out that sodium silicofluoride, sodium hydrogen fluoride, oxalic acid and ammonium persulphate, if used in concentrations of not more than 0·01 per cent., have no effect on the tensile strength of the goods being laundered. Incidentally iron stains are best removed by oxalic acid and sodium acid fluoride.

Harkins and Clark (*J. Amer. Chem. Soc.*, 1925, **47**, 1854) found that small amounts of alkali added to 0·1 M.-sodium nonylate solution increased the surface tension from 20·2 dynes per cm. to 45·4 dynes per cm., but further additions caused a linear decrease. Powney (*Trans. Faraday Soc.*, 1935, **31**, 1510) made similar observations with solutions of the soaps, sodium oleate and potassium laurate. With the former, the maximum surface tension occurs at pH 10–11, and with the latter, at pH 7–9.

The detergency of soap solutions is interrelated with the magnitude of the interfacial tension, which exists between aqueous soap solutions and immiscible liquids, such as benzene and xylene. The addition of alkali to soap solutions lowers the interfacial tension against benzene. Neutral salts also have an effect (Shorter and Ellingworth, *Proc. Roy. Soc.*, 1916, **92A**, 231 ; Dubrisay, *Compt. rend.*, 1924, **178**, 1976 ; Harkins and Zollman, *J. Amer. Chem. Soc.*, 1926, **48**, 69). Powney and Addison (*Trans. Faraday Soc.*, 1938, **34**, 356), using xylene, found that a rapid lowering in interfacial tension occurs above pH 8, and that the precise changes depend on the pH.

By means of the glass electrode, Powney and Jordan (*ibid.*, 1938, **34**, 363) measured the degree of hydrolysis of soap in solutions of decreasing concentration. As the solution becomes more dilute the hydrolysis passes successively through a maximum and then a minimum, and thereafter undergoes progressive

hydrolysis. This progressive hydrolysis is such as would be expected of a salt of a strong base and a weak acid. At the higher concentrations, the properties conform with those of a colloidal electrolyte (*cf.* McBain, *J. Amer. Chem. Soc.*, 1920, **42**, 426 ; Lottermoser and Ghose, *Kolloid Beihefte*, 1937, **45**, 253).

According to Snell (*Ind. Eng. Chem.*, 1933, **25**, 1240), the desirable properties of alkaline detergent solutions are : (i) high initial pH, limit 11·5, (ii) large neutralising value above that of soap, *i.e.*, above *ca.* pH 10·2, (iii) the ratio of titratable alkalinity above pH 10·2 to that above pH 4·0 should be as near unity as possible. The last property ensures that the greater part of the " builder " employed is available for neutralising the dirt and soil present on the textiles.

Regarding the newer detergents Götte (*Koll.-Z.*, 1933, **64**, 222, 327, 331) points out that the maximum scouring efficiency is not reached until the pH is raised to 10. Jones and Smith (*Amer. Dyestuffs Rept.*, 1934, **23**, 423) stresses the dependence on pH of such detergents as sulphonated alcohols, but points out that they can be used in neutral solutions with delicate fibres, such as cellulose acetate, which are attacked by alkali.

Shaving cream of the " brush-less " type has a pH of 7·2, that of the " brush " type is 9·4. Fash (*Ind. Eng. Chem.*, 1937, **29**, 68) points out that oxygen corrosion is greater at pH 7·2 than at pH 9·4, and that the corrosion of razor blades can be lessened by including in the " brush-less " cream a passivating agent, *e.g.*, potassium chromate.

Jinkings and McGraghan (*J. Soc. Chem. Ind.*, 1937, **56**, 238T) find that solutions of sodium perborate, $NaBO_3,4H_2O$, are stable within the range pH 6–8, but that, with increasing pH they become very unstable. Soap, however, provides some stabilising action.

11.   Dentifrices.

It is likely that the hydrogen-ion concentration of dentifrices is a factor which merits attention, for below pH 5·5 calcium phosphate becomes soluble, and thus it may be that any tooth-paste of a low pH remaining in the crevices may be particularly destructive. Maclean (*Proc. Roy. Soc. Med., Sect. Odont.*, 1927, **20**, 873) experimenting on the possible initiation of caries by acid forming bacteria when grown *in vitro* in presence of teeth, found that unless an acidity greater than that indicated by pH 5 is attained penetration of the enamel is very slow.

12. Antiseptics.

Bittenbender, Degering and Tetrault (*Ind. Eng. Chem.*, 1939, 31, 742) have shown that the efficiency of certain antiseptics towards bacilli is regulated by the pH of the solutions. Table 228 gives the lethal doses at pH 3 and pH 7 for *Staphylococcus aurens* and *B. coli* of a number of antiseptics.

TABLE 228

	Staph. aurens.		B. coli.	
	1 part Antiseptic at pH 3	pH 7 in	1 part Antiseptic at pH 3	pH 7 in
Phenylmercuric nitrate . .	100,000	10,000	400,000	30,000
Merthiolate	75,000	10,000	100,000	5,000
Tincture of iodine . . .	4,000	1,000	4,000	1,500
Phenol	90	60	100	75
Hexyresorcinol	100,000	3,000	100,000	5,000

13. Tobacco.

Tobacco contains basic substances, such as albuminoids, nicotine and ammonia, in combination with various acids, *viz.*, *l*-malic, citric, *d*-tartaric, fumaric, maleic, succinic, lactic, acetic and malonic. Both the nicotine and the protein contents of tobacco depend on the nature of the plant, which in turn depends on the soil, the fertilisers used and the climatic conditions. Light coloured, thin leaves usually contain little nicotine. The content of nicotine varies with the part of the plant. It is smaller in the flower than in the upper leaves and it increases along the leaf from stem to tip, according to the length of time it has been exposed to the sun. The stalks are generally low in nicotine; less than 0·5 per cent. This accounts for the high nicotine contents of cigars made from leaves from which the stalks have been removed.

According to Pyriki and Dittmar (*Z. Unters. Lebens.*, 1931, 61, 216) oriental tobacco does not lose any of its basic constituents when dried at 50°, but drying above 95° causes volatilisation of nicotine, leaving 0·2–0·4 per cent. of nicotine behind. The quality of fermented tobacco improves from the lower to the higher leaves of the plant. Since the hydrogen-ion concentration of the cell sap increases with the higher position of the leaf, it follows that the pH of good quality tobacco is lower than that of the inferior qualities. There is a tendency for the pH of

tobacco leaves to diminish as they tur;n brown. Andreadis and Toole (*ibid.*, 1934, **68**, 431) found that the content of nicotine increases from stalk to tip and from midrib to margin. Owing to the gradual increase in the ratio of acids to nicotine, the *p*H diminishes from stalk to tip‹ and from midrib to margin. The *p*H of ordinary tobacco lies between 4·7 and 5·8, depending on the age of the leaves, their position on the stem and their ripeness.

The *p*H of high quality tobacco is lower than that of poorer quality. Pyriki (*ibid.*, 1932, **64**, 273) considers that the high acidity produces a mildness in the smoke as the result of the combination of the nicotine and other basic substances with the acids. Cigarette tobacco ranges from *p*H 4·95 to *p*H 5·29, the better quality being of *p*H near to the lower limit. Storage of cigarettes in sealed packets causes lowering in *p*II, whereas loose cigarette tobacco tends to increase in *p*H.

The accurate measurement of the *p*H of tobacco is thus a matter of some importance, and according to Brückner (*Der Biochemie des Tabaks*, Berlin, 1936), it should be determined within 0·01-0·02 *p*H. The method described by Pyriki (*Z. Unters. Lebens.*, 1939, **77**, 157) is to stir 0·5 gram of powdered or shredded tobacco with 10 c.c. of distilled water for one minute and, after adding saturated quinhydrone solution and stirring for a half to one minute, the *p*H measurement is made. For this purpose, powdered tobacco is preferable, the sample being dried at 30° for three hours and then powdered. Pyriki's experiments showed that tobaccos of *p*H 5·5 can be dried at 50° for three hours with little change in *p*H, and that lower *p*H tobaccos are not appreciably affected by drying at 95°. A Java cigarette tobacco of *p*H 6·5 was susceptible to drying, as far as change in *p*H was concerned, even when dried over fused calcium chloride at room-temperature.

The acids, except oxalic, present in tobacco leaf may be titrated electrometrically by a procedure devised by Pucher, Vickery and Wakeman (*Ind. Eng. Chem., Anal. Edn.*, 1934, **6**, 140). The leaves are powdered, brought to *p*H 0·6-0·9 by means of sulphuric acid, and extracted with purified ether using an extraction thimble for 17 to 20 hours. The extract is adjusted to *p*H 7·8 with sodium hydroxide and then titrated, using the quinhydrone electrode, with nitric acid, to *p*II 2·6. The authors considered that in this method the extracted acids, except oxalic, amount to 90 per cent. of the total, and the titre is therefore multiplied by 100/90.

14. Rubber Latex.

The regulation of the hydrion concentration of rubber latex has been found to be of importance in effecting coagulation. (De Vries and Beumée-Nieuwland, *Arch. Rubbercultuur*, 1928, **12**, 454 ; van Harpen, *ibid.*, 1929, **13**, 44.)

The pH of normal latex (30 per cent. solids) lies between 8·64 and 11·96 (Jordan, Brass and Roe, *Ind. Eng. Chem., Anal. Edn.*, 1937, **9**, 182). When diluted to 4 per cent. solids, the latex is completely coagulated at pH 0·8, partially coagulated between pH 0·8 and 1·0, completely dispersed between pH 1·0 and 3·5, partially coagulated between pH 3·5 and 3·8, completely coagulated between pH 3·8 and 4·83, again partially coagulated between pH 4·83 and 4·91, decreasingly flocculated from pH 4·91 to pH 5·30 and again completely dispersed at higher pH values. As coagulants, acetic acid, formic acid, alum, sodium acid formate, guanidines and allyl- and benzyl- amines are employed (Fullerton, *Rubber Res. Inst., Malaya, Quart. J.*, 1930, **2**, 156).

A method of ascertaining the condition of maximum stability of latex solutions is to titrate the rubber latex with potassium hydroxide to the inflexion at pH 10·7–11. The " potash number " obtained therefrom, *viz.*, the number of grams of KOH required per 100 grams of latex solids, gives the amount of potash which must be added to obtain maximum stability. This method refers to latex solutions containing zinc oxide but no buffering agents. When glue or casein is admixed with the latex the additional potash will also be indicated by titrating to pH 10·7–11·0 (Jordan, *India-rubber J.*, 1938, **95**, 794).

According to I. G. Farbenind. *A.-G.* (B.P. 309,245), latex is coagulated with acids or acid-producing substances in the presence of an organic substance, which possesses soap-like properties and reduces the surface tension of the latex but which is not decomposed by acid to form insoluble products. If the latex is acidified below pH 2 quickly, either before or after the addition of such a substance, the whole mass will set to an irreversible jelly.

In order to impregnate cotton fabrics with rubber latex, the pH of the latex and the fabric should be equal ; in any case the fabric should be rendered sufficiently alkaline to prevent the premature coagulation of the latex through the loss of ammonia (B.P. 405,311–3). Greenup (*Ind. Eng. Chem.*, 1931, **23**, 688) finds that ammonia preserved latex produces satisfactory deposits on alundum moulds (in the form of shoes, bottles, etc.) when the pH of the latex is adjusted to 6·1 by means of boric acid.

According to Szegvari (B.P. 357,740), conditions for uniform
electrophoretic deposition are realised when the latex has a pH
of 9–12 and a specific resistance between 50 and 1000 ohms/sq.
cm.

The Wulff colorimeter (see p. 287) is stated by Mackay
(*India-rubber J.*, 1930, 79, 353) to be particularly useful for rubber
latex. When accurate pH values, however, are required indicator
methods should be avoided in view of the high protein errors.
The hydrogen electrode may be used but occasionally difficulties
may arise. The glass electrode is satisfactory, so also is the
quinhydrone electrode up to pH 7–8.

Commercial types of neoprene latex often contain an excess
of alkali, which Livingston and Walsh (*Ind. Eng. Chem.*, 1946, 38,
1262) find cannot be satisfactorily controlled at any desired pH
by means of either concentrated or dilute solutions of acids
having dissociation constants greater than 5×10^{-6}. Yet
amino-acids of which K_a is as high as 10^{-2}—10^{-5} do not cause
coagulation even in concentrated solution. They prefer glycine
as the pH regulator and its use in the manufacture of foam sponge
overcomes variations in the gelation properties of neoprene latex.

15. Plastics.

The production of synthetic resins by the action of formal-
dehyde on soya bean protein is best carried out at, or near, its
isoelectric point. The resin thus formed is least adsorptive
towards water, and also possesses maximum thermo-plasticity
(Brother and McKinney, *Ind. Eng. Chem.*, 1938, 30, 1236).

Soya bean protein can be extracted with acid. The maximum
yield is obtained at pH 2 and the minimum at pH 4·2. Extraction
with alkali increases from pH 7 upwards (Smith and Circle, *ibid.*,
p. 1414).

16. Foams as Fire Extinguishers.

Foams are becoming of importance in combating fires and
especially oil fires. The foam is formed by the interaction of
two solutions, one of which contains sodium bicarbonate and a
foaming agent, *e.g.*, glue, glucose, liquorice extract, saponin
extract, and the other solution containing aluminium sulphate,
sometimes with very small amounts of sulphuric acid (*cf.* Swift,
Ind. Eng. Chem., 1924, 16, 580). The foam produced by the
evolution of carbon dioxide will be rendered more stable if the
bubble walls, reinforced by the gelatinous aluminium hydroxide
precipitated within them, are not rapidly ruptured by the too
sudden production of gas. As emphasised by Swift, " a good

foam must be produced in large volume, must be tenacious so as to withstand mechanical abuse, must be fluid enough to flow freely over a burning surface of oil, but stiff enough to adhere to a vertical surface when used on other fires, and must not wilt rapidly when exposed to the flames." In the opinion of the author, the efficiency of such foams rests on the pH value set up by the two solutions on mixing, both in regard to the rate of gas evolution and to the quality of the precipitated aluminium hydroxide, *i.e.*, if the pH value of the mixed liquids must exceed pH 4·1 at which aluminium hydroxide just begins to separate.

17. Explosives.

Explosives of the nitro-ester type, *e.g.*, nitro-cellulose, nitro-glycerin, are apt to hydrolyse and thereby to lose their stability. Hansen (*Förh III nord kemistmötet*, 1928, 227) has proposed a rapid method of testing the stability of smokeless powders by measuring the change in pH after heating at 110° for 8–10 hours. (See also *Metz.*, *Z. ges. Schiess- u. Sprengstoffw.*, 1929, **24**, 245, 291, 335.)

The neutralisation of nitro-cellulose and nitro-glycerin needs careful pH control. Instead of using sodium carbonate, Norton and Boyd (U.S.P. 1,912,399) employ a solution of salts at pH 8·3–12·0, *e.g.*, sodium phosphate or borate.

18. Crystalline, Non-caking Ammonium Sulphate.

A coarse crystalline and more stable ammonium sulphate, suitable for use as a fertiliser, may be obtained by crystallising in the presence of 0·0003–0·07 per cent. of aluminium salts, *e.g.*, the oxalate, at pH 5·8–7·0 (I. G. Farbenind. *A.-G.*, B.P., 445,120 ; 435,007 ; *Chem. Trade J.*, 1936, **98**, 385).

19. Scrubbing Boiler Flue Gases.

Flue gases, containing 0·05–0·20 per cent. SO_2 and 0–10 per cent. SO_3, are passed through a cream of milk of lime. By maintaining the pH at 6·3 $\pm$ 0·2 the solubility of the calcium sulphite formed is reduced. Such a pH reduces the corrosion of steel towers and pipes to a minimum. It also makes possible the almost complete removal of carbon dioxide as $Ca(HCO_3)_2$ (Nonhebel, *Trans. Faraday Soc.*, 1936, **32**, 1291).

20. Colloidal Carbon.

Wiegand (*Ind. Eng. Chem.*, 1937, **29**, 953) points out that the pH of colloidal carbon serves as a means of assessing its

quality.   He determines the pH by bo'ling 1 part of carbon with
3–10 parts of water for at least 15 minutes, and then tests the
supernatant liquid. As a rule, the pH values lie between pH 2·6
and 4·6, although bone black gives pH 9·0 and acetylene black
pH 8·2.   Carbon blacks for use in inks and paints are of low pH,
but the use of too low pH carbons (2·6–3·0) may lead to slow
drying.   Rubber carbons are of pH 3·3–4·6.   Slow vulcanising
carbons have pH values lower than those which cure rapidly.

NAME INDEX to VOLS. I and II

The numbers printed *in italics* refer to Vol. I ; those in ordinary type to Vol. II